

**"THE STUDIES ON KINETICS & MECHANISM  
OF OXIDATION OF DIOLS & CYCLIC  
ALCOHOLS BY Ce (IV) SULPHATE IN ACIDS  
MEDIUM"**

A THESIS  
SUBMITTED TO THE  
**BUNDELKHAND UNIVERSITY JHANSI**  
FOR THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**  
IN CHEMISTRY

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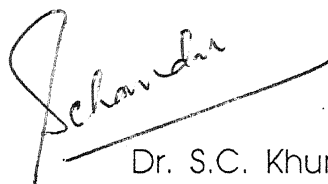
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POST. GRADUATE DEPARTMENT, OF CHEMISTRY  
D.V. COLLEGE ORAI (INDIA)  
AFFILIATED TO BUNDELKHAND UNIVERSITY  
JHANSI  
**2002**

## SUPERVISOR'S CERTIFICATE

It is a great pleasure to certify that the thesis in hand titled "The studies on kinetics and mechanism of oxidation of diols and cyclic alcohols by Ce (iv) sulphate in acids medium". submitted by Ms. Neeti Tripathi for the fulfillment of doctor of philosophy in chemistry is her own work. She has been carried out very hard work under my supervision and guidance.

This thesis is her original contribution. I wish her bright future.

Date : 15.12.2002



Dr. S.C. Khurana  
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## OBLIGATION

I would like to mention that I feel deeply compeled and obliged to all those who have made this work possible.

I wish to erepress my deepest and hearty gratitude to my research guide Dr. J.P. Pachauria & now Dr. S.C. Khurana as without his inspiration, guidance and suggestion this work would not have reached to this point of fruitation.

I am extremely grateful & myhearty thanks to Dr. I.M. Beg, Dr. K.C. Gupta, Dr. S.K. Srivastava, Dr. G.S. Niranjana, Dr. Rajendra Nigam, Dr. Salendra Gupta & rest of loving staff. for their fruitful suggestion.

I am very much thankful to my in-laws, my parents, my sister & my lonely brother. who motivated me to complete this work.

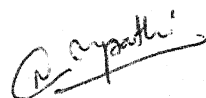
My warmest thanks are to my husband Mr. G.S. Mishra for this moral & intellectual support. My deepest obligation goes to my Niece Neha Tripathi, Preeti Misra & my lonely child Palak Mishra.

At the end, I am thankful to Mr. Narendra Mohan and his brother who typing out my research work on Computer with special interest and very carefully.

Thanks to all.

Dated :

10/12/02



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# **CHAPTER-I**

## **INTRODUCTION**

## Introduction

### 1- Cerium (IV) ion as Oxidant

Reaction involving oxidation and reduction are amongst the most common processes. Simply the cerium salts have been used for the estimation of the organic and inorganic compounds.

Besides this perchloride acid<sup>1</sup> lead tetra acetate<sup>2</sup>, trivalent manganese<sup>3</sup>, hexavalent chromium, sodium bisulphate<sup>4</sup>, heptavalent manganese<sup>5</sup>, osmium tetroxide<sup>6</sup> and ferri cyanide have also been used as oxidation.

A systematic study of Ce (IV) as an oxidant in analytical estimation has been firstly reviewed in 1942 by G.F. Smith and two more views were published in 1958.

Recently these reaction have been studies in detail and a review on Ce (IV) ion oxidation of organic compounds has been published by W.H. Richardson in 1965.

In the present study cerium (IV) has been chosen because this oxidant can be used in different acid media as sulphuric acid perchloric acid and Nitric acid and due to the fact that oxidation of Ce (IV)/ Ce (III) couple is independent on the anion of the acid used. This has been shown in the following table.

Table 1.1

Cerium (III)- Cerium (IV) half cell potentials

Acid (M)	Measured E			
	HClO <sub>4</sub>	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCL
1.00	1.70	1.61	1.44	1.28
2.00	1.71	1.62	1.44	
4.00	1.75	1.61	1.43	
6.00	1.82	-	-	
8.00	1.87	1.56	1.42	

It is thus seen that in case of perchloric acid the oxidation potential increases with increasing concentration of acid but on the other hand the oxidation potential is decreased on increaseng the conc of other acids, which considered to be due to the complexing of cerium (IV) ion with nitrate B and sulphate ion has been reported.

The oxidation of cyclic alcohol by Ce (IV) proceed with the formation of intermediate 1:1 complex which is suspected from the appearances of the red shift invisible spectra. The kinetic data given by Ardon have been confirmed this suspicion. The oxidation of alcohol by quadrivalent cerium in aq. H<sub>2</sub>SO<sub>4</sub> medium was studied by shatt. K and Nand K.C.

Prasad and Ghosh<sup>7</sup> have reported the oxidation of ethylene glycol by ceric sulphate in sulphuric acid medium using Ce (III) as catalyst.

The empirical formula of Ce (IV) complexes with n-sec. and tert. Butanol were determined from spectrophotometric measurements and in all cases a 1:1 ratio of cerium and alcohol was observed in the complexes.

Silver (I) catalysed oxidation of diaacetone alcohol by Ce (IV) in  $H_2SO_4$  medium is reported by Rao K. Nangeswar, Sondu S., Sethuram B.

Recently the kinetics of oxidation of substituted L- phenyl ethyl alcohol aromatic secondary alcohols and cycloalcohols have been studied and the oxidation is shown to proceed via the well known Ce (IV) alcohol complex formation in the ratio 1:4 ceric cerium oxidant of resorcinol and Ce (IV) oxidant of meyesol is reported by yadav R.L. and Verma R.G.

Bihari kuni, Panday N.N. and khann R.K. have studied the oxidation of hexanol and diol by Ce (IV) in  $H_2SO_4$  medium. Kinetics of the oxidation of  $\mu$ - oxobis (aqua bis (2, 2' - bipyridine) ruthenium (III)) by L- cysteine in aqueous solution is reported by J. femi iyun.<sup>8</sup>

P. Narasimha char, S. Sondu, B. Sethuram & T. Navaneeth Rao<sup>9</sup> have investigated the kinetics of Ru (III) catalysed oxidation of chalcones by acid bromate in  $H_2SO_4$  - H O Ac medium kinetics of Ru (III) chloride catalysed oxidation of chalcones and some substituted chalcones by acid bromate have been studied in acetic acid - sulphuric acid medium in the temperature range 303 - 318 K. The reaction is first order each in (Chalcone) and (Ru (III)) and zero order each in  $(H^+)$  and  $(BrO_3^-)$

Kinetics and mechanism of Ru (III) catalysed oxidation of substituted cinnamic acids by cerium (IV) is studied by H.P. Panda & B.D. Sahu.<sup>10</sup>

Ruthenium (III) catalysed oxidation of substituted cinnamic acids by (Ce (IV)) in aqueous acetic acid - sulphuric acid medium follows a complex rate law, the reaction being Zero order in (Ce (IV)), first order in (Ru (III)) and fractional order in (substrate). Ruthenium (III) catalysis in the study of oxidation kinetics of a large number of organic compounds by a variety of oxidants is now well established.

The kinetics of Ce (IV) oxidation of ortho and meta-methoxymandelic acids in sulphuric perchloric acid media is reported by A. Seza sarac & Ayten Gocmen.<sup>11</sup> The kinetics of oxidation of O- and M- - methoxy- mandelic acids to the corresponding methoxy bezaldehydes by Ce (IV) has been studied spectrophotometrically in  $\text{H}_2\text{SO}_4$  -  $\text{HClO}_4$  media, in the range of 0.08 - 0.42 mol  $\text{dm}^{-3}$   $\text{HSO}_4^-$  at ionic strength of 2.0 mol  $\text{dm}^{-3}$ . The results indicated that one mole of hydroxy acid required two mole of Ce(IV) for oxidation.

Rashmi Saxena, Sushma Gupta and santosh K. Upadhyay<sup>12</sup> investigated the kinetics and mechanism of ruthenium (III) catalysed oxidation of aminoalcohols by N- Bromo succinimide in perchloric acid media. A first order dependence of rate in (NBS) in case of primary aminoalcohols and a second order dependence of rate in (NBS) in case of secondary/ tertiary aminoalcohols have been observed.

The kinetics of oxidation of chloroacetic acids by Sodium N-bromo-P- toluene sulphonamide (bromamine- T) in HCl medium and catalysis by Ru (III) ion is studied by Venkatesha B.M.<sup>13</sup> Ananda S. and Mahadevappa D.S. Ruthenium (III) catalysed oxidation of mono, di and trichloroacetic acids by bromamine- T (BAT) in acid medium has been studied at 40°C.

Ch. Sanjeeva Reddy<sup>14</sup> & Vijaya kumar. T. investigated the kinetic and mechanistic study of ruthenium (III) catalysed oxidation of oxalic acid by acid bromate.

The kinetics and mechanism of iridium (III) catalysed oxidation of formic acid by cerium (IV) in aqueous sulphuric acid media is studied by Asim K. Das and mahua Das. The kinetics of oxidation of formic acid by cerium (IV) in the presence of iridium (III) ( $[Ca\ 10^{-6}\text{ mol dm}^{-3}]$ ) in aqueous sulphuric acid media, have been followed at different temperatures (30-50°C) at fixed  $[H^+]$  under the conditions  $(HCO_2H) \gg (Ce^{IV})_T \gg (Ir)_T$ , the rate of disappearance of cerium (IV) in the reaction has been found to be first order with respect to cerium (IV).

Rajani K. Mohanty<sup>16</sup>, Mahua Das & Asim K. Das have investigated the kinetics mechanism of iridium (III) catalysed oxidation of ethanol by cerium (IV) in aqueous sulphuric acid media.

Kinetic studies on the oxidation of ethanol by cerium (IV) in perchloric acid media have been reported by Ardon.<sup>17</sup> Different metal ion catalysts have been used<sup>18</sup> in oxidation reactions by cerium (IV) in aqueous sulphuric acid media. Among the different metal ions, ruthenium (III)<sup>19-24</sup> have been found to be highly efficient.

Sudhin K. Mondal.<sup>25</sup> Dalia Kar, Mahua Das & Asim K. Das. Deptt. of chem., Visva-Bharti, Santiniketan proposed the kinetics and mechanism of iridium (III) catalysed oxidation of butane 2-ol by cerium (IV) in aqueous sulphuric acid media.

The kinetics and mechanism of chromium (III) catalysed oxidation of ethanol by cerium (IV) in aqueous sulphuric acid media have been proposed by Asim K. Das, Sudhin K. Mondal & Dalia Kar<sup>26</sup>.



The Kinetics and mechanism of the ruthenium (III) catalysed oxidation of some glycols by cerium (IV) in sulphuric acid medium have been investigated by Bharat Singh<sup>27</sup> Meera Singh & Deep Mala Kesarwani. The reactions are found to be zero order with respect to cerium (IV) ion and hydrogen ion. Zero order dependence of (Ce (IV)) clearly suggests its involvement in the fast step first order kinetics with respect to each glycols and ruthenium (III) chloride has been observed.

The kinetics & mechanism of glycols have been found by various other journals<sup>28-35</sup>.

Ru (III) Catalysed oxidation of diols and cycloalcohols by phenyl iodose acetate is reported by Pati S.C., Dev B.R..

Tondon R.K. Manibala, K Singh H.S. have investigated the mechanism of Ru (III) catalysed oxidation of cyclopentanol, cyclohexanol and cycloheptanol by Ce (IV) sulphate in sulphuric acid medium. Satprakash and sethuram the kinetics of oxidation of ethyl and benzyl alcohol with ceric sulphate in sulphuric acid and suggested that the neutral ceric sulphate molecule is the reactive species.

The kinetics of oxidation of some aliphatic ketones and aldehydes by ceric sulphate has been reported in detail by Shorter and Hinselwood, Suprun V. Ya, Dinitri Shin R.T. have studied the oxidation of aliphatic saturated and unsaturated aldehydes by Ce (IV) sulphate in  $H_2SO_4$  Medium. Hargreaves and sutcliffe studied the oxidation of formaldehyde by Ce (IV) in perchloric acid and sulphuric acid, in case of acetaldehyde, formic acid was produced.

In relation to Belousov-Zhabotinski reaction Trendle Ludouit, Keplan peter<sup>34</sup> reported the oxidation of 2-4 pentanedione with Ce (IV) ions.

Venkatash krishna and Santappa M<sup>34</sup>, have also studied the oxidation of acetone and ethyl methyl ketone by Ce (IV) perchlorate and shown that enol form favour as reactive species in the case of ketones and kinetics of oxidation of cyclic ketones by Ce (IV) in aqueous sulphuric acid medium has been studied by Bihari and coworkers.

Simple aliphatic acids (formic, acetic and propionic) are not oxidised by ceric sulphate in refluxing dilute sulphuric acid very recently Wella and Russain have studied the kinetics of oxidation of formic acid by aquo-cerium (IV) ion in aqueous perchlorate media. Their results have shown that the slow oxidation of formic acid by Ce (IV) proceeds by inner sphere mechanism in the series of decarboxylic acid. Only oxalic acid and malonic acid have been oxidised by Ce (IV).

Krishna and tiwari in 1961 have studies the kinetics of oxidation of mandelic acid (a) Maliec and lactic acid by ceric sulphate. Sangupta has also studied the kinetics of oxidation of tartaric acid (a) glycolic acid (b) citric acid and glyoxylic acid (c) by Ce (IV) ion. Recently 1:1 cerium (IV) tartaric acid complex is confirmed spectrophotometrically by Drake and Nutt.

Kinetics and Mechanism of p- bromomandilic acid (a) D.L. atrolactic acid-2 hydroxy butylel acid <sup>45</sup> (b) substituted glycolic acid<sup>46</sup> (c) and p-cloromanadilic acids by Ce (IV) in sulphuric acid has been studied by Gupta (d) etal.

Hill and MC Auley reported the oxidation of some 1- merchapto carboxylic acid by Ce (IV) between 0°C and 25°C using stopped flow technique.

Behari Kuni, Pachauria J.P. (a) have studied the oxidation of

acrylic methacrylic and crotonic acid by Ce (IV) in  $\text{H}_2\text{SO}_4$  medium is reported by Behari Kuni, Kumar Pradeep and Pachouria J.P.<sup>50</sup> (b).

Kinetics of oxidation of ketoglutaric acid with Ce (IV) was investigated by Trendle Ludovet in relation to Belousov Zhapatinski reaction, kinetics and oxidation of Ag (I) catalysed oxidation of acrylic acid by per oxidisulphate ion is reported by Agrawal Giridharilal, kinetic studies of Maleic acid and fumaric acid by Panton's reagent have been complete by Ahmad, Iftikar and El patih oxidation of phenyl acetic acids by Ce (IV) perchlorate is studied by Vasudevan R., Subramaniam. P..

Kinetics and mechanism of oxidation of alcohols by Ceric ammonium nitrate the main product of the oxidation of secondary alcohols by (AN is the corresponding acetone).

The anox is 1st order to the oxidant but exhibits mechanistic - minter type kinetics. As to the alcohol, the formation constant of the alcohol. Ce (IV) complex and its thermodynamic parameters were called.

The rate of decomposition of the complex and the activation parameter were also evaluated the rates of decomposition the complex correlate with taft values with log-ve toxm composition the retardation of rate with increasing oxidicity has been explained by formation of mechanistically inactivated protonated alcohol. The protonated constant for the various alcohols were called the presence of small primary kinetics isotope effect  $k_H/k_D = 2.3$  confirms that the reaction involves AC - H bond in monosymmetric T. S Malthus Dwarka, Agarawal Anupma, Banerji Kalyan.

Kinetics and mechanism of Ru catalysed oxidation of lactic acid

by peroxadiphosphate. The kinetics was studied of Ru (III) in ag. acid medium, He rate dependence on (H<sup>+</sup>) reveals that the active oxidising species in the oxidation could be H<sub>3</sub>P<sub>2</sub>O<sub>8</sub>. The Ru (III) catalysis of (PP-La) rection is explained in terms of a 1:1 complex formation between Ru (III) and 2 A wich later reacts with PF bimolecularly to give the products Jagannathan J. Rao M., Anand, Sethuram R., Rao T, Navaneeth.

Kinetics and mechanism of oxidation of some alcohols by osmium tetroxide. First order rate const. for the oxidation of 2- methyl propanl and 2- butanol by an alcoholic solution of H<sub>2</sub>SO<sub>4</sub> were detd. from UV spectral data activation perameters were calculated. The rate determining step involves CuSO<sub>4</sub>, COH creation with alcohol. Singh Bharat<sup>66</sup>, Singh A.K.<sup>67</sup>, Singh M.B.<sup>68</sup>.

## 2- Oxidation of Alcohols by Ce (IV)

Several workers have studied the mechanism of oxidation of diols and cyclic alcohols by cerium (IV) in acidic media. They have reported the first order dependence of Ce (IV) concentration. A plot of 1/K (observed) versus 1/alcohol was found to be linear. They have proposed the complex formation between cerium (IV) and organic substrate according to the following mechanism.



From the above mechanism the following rate law has been derived.

$$\frac{-d (\text{Ce (IV)})_T}{dt} = \frac{K (\text{Ce (IV)})_T \text{CyOH}}{1 + K_T \text{CyOH}} \quad - (3)$$

Where  $\text{Ce (IV)}_T$  is  $\text{Ce (IV)} + \text{Ce (IV) Complex}$ .

The complex between Ce (IV) and alcohol was also confirmed by these authors from the appearance of red shift in the visible spectrum on adding glycol to cerium (IV) Littler - 18 and waters have also reported that the increase in glycol concentration decrease the rate of the reaction. On the other hand ceric sulphate oxidation of cyclohexanol does not show a decreasing rate with increasing alcohol concentration. The product of oxidation in the case of glycol is 90% acetaldehyde whereas in the case of cyclohexanol the oxidation product is cyclohexanone.

Prasad and Ghosh have reported the oxidation of glycol by ceric sulphate in sulphuric acid medium using chromic as catalyst.

The empirical formula of Ce (IV) complexes with n-sec and tert-butanol were determined from the spectrophotometric measurement and in all cases a 1:1 ratio of cerium and alcohol was observed in the complexes.

The Kinetics of mercuric chloride catalysed oxidation of propylene alcohol to acetone by cerium (IV) in sulphuric acid is studied by Anantraman and Nair. Similarly oxidation of butylene alcohol<sup>23-24</sup> to acetone and acetone to formic acid by ceric sulphate in sulphuric acid

in the presence and absence of mercuric chloride has been studied.

Krishna and Tiwari in 1961 have studied the kinetics of oxidation of mandelic acid dl- malic lactic acid by ceric sulphate.

Recently spectrophotometric kinetic study cerium (IV) tartaric acid reaction in sulphuric acid by Drake and Nutt has confirmed 1:1 cerium (IV) tartaric acid complex which is subsequently decomposed by unimolecular mechanism.

Mc Auley has studied the oxidation of thiourea and its N- substituted derivatives at  $H^+ = 0.5 \text{ m}$  between 5-25° using stopped flow method.

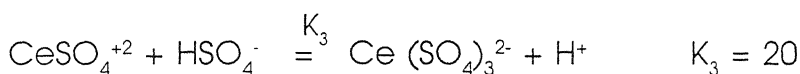
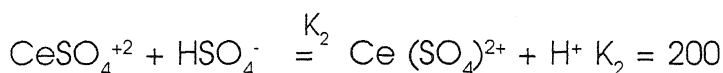
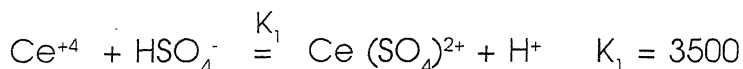
The kinetics of oxidation of dimethyl sulphoxide by periodate catalysed by Os (VIII) and Ru (III) was studied by Radha Krishna Murti and coworkers.

The oxidation of 1:2 glycols and related compounds have been reported by Conant Aston and their mechanism of oxidation has been studied by Littler and Waters and co-workers. Krishna & coworkers studied in details the oxidation of butane 1 : 4 diols pentane 1 : 5 diols hexane 1 : 6 diols etc. and the oxidation of o, p, m cresol by cerium (IV) was studied by J.P. Singh and co-workers.

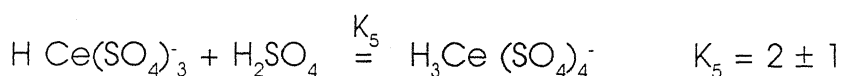
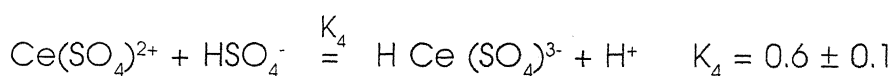
Osmium tetroxide catalysed oxidation of fumaric and malic acid with potassium perchlorate was first studied by Murry. Hoffman<sup>38</sup> and Milas<sup>39</sup> suggested that the oxidation involves complex formation osmium tetroxide and unsaturated acids. Cric ges has studied the addition of osmium tetroxide with olefines. He showed that each olefine molecule contains one molecule of osmium tetra oxide.

### 3. The reactive species of Ce (IV) in presence of aqueous sulphuric acid-

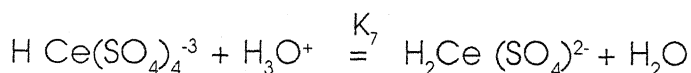
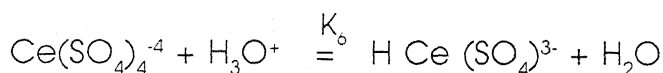
Ce (IV) exists in various forms according to Hardarck and Roberson in sulphuric acid solution of 2 molar at constant ionic strength.

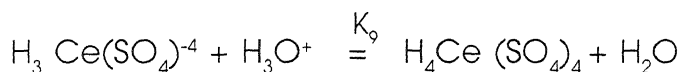
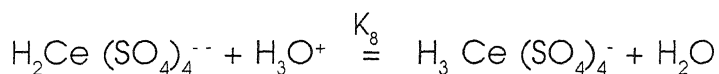


Buganko and Kuanlin have investigated more recently the nature of Ce (IV) spectrophotometrically in 0.1 to 17.6 sulphuric acid ionic concentration being not constant. The equilibrium at  $20 \pm$  is shown below.

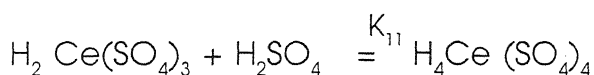
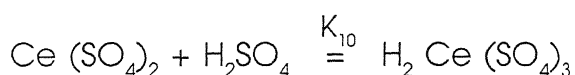


They have suggested the  $\text{Ce}(\text{SO}_4)_2$  and  $\text{H Ce}(\text{SO}_4)_3^-$  are prominent species upto 2 M and  $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$  exists above 2 M  $\text{H}_2\text{SO}_4$  Hargreaves and Sutcliffe suggested in addition following equilibrium to explain the mechanism of certain reactions.





But the equilibrium constants have not been calculated though they have been useful in deriving some mechanism in addition to above equilibrium following equilibria were also proposed.



In Oxidation of ethylene glycol with cerium sulphate Bhagwat and Co workers and Mehrotra and Shukla suggested reactive species as cerium sulphate. On the other hand Mac Auley and Brubaker Mehrotra and Sankhle, Guilbeilt and Mc Curdy Suggested reactive species as  $\text{Ce}(\text{SO}_4)^{+2}$ .

Kaizarman and Rasmussen in the oxidation of pinacole by Ce (IV) have suggested  $\text{Ce}(\text{SO}_4)_3^{-2}$  as reactive species. Gupta and Grover have suggested  $\text{Ce}(\text{OH})^{2+}$  as main reactive species in the oxidation of bezilic acid with Cerium (IV) sulphate.



#### 4. Importance of the present study

The study of the mechanism of a chemical reaction employing reaction kinetic data has been a subject of interest to several chemists because it has vast applications in the understanding of the salient, electronic, structural and stereo chemical features of a chemical process. With the help of the kinetic data it has been possible to control the course and products of a reaction and thus the conditions required for favouring a desired product can be successfully predicated. A knowledge of mechanism by which the reactants are changed to the product is of great value and the study of the kinetics of the reaction coupled with other techniques forms one of the most satisfactory ways for obtaining information about the mechanism involved in a particular reaction. Kinetic approach required consideration of deep and detailed pictures of process and is more explanatory in character.

Kinetics is concerned with the detailed study of the rates of chemical reactions and is time dependent, order of reaction with respect to the reacting species, effect of ionic strength dielectric constant of the medium, effect of pH and non electrolytes etc. are some of the important factors which are helpful in elucidation of the mechanism of reaction in solutions. Thermodynamic parameters viz energy of activation and entropy of activation also provides the information about the mechanism. In catalysed reactions, several short lived intermediates may be formed involving the catalyst and thus a mechanism of a catalysed reaction may be different from that of the uncatalysed

reactions, although the end products may be the same. In addition, characterisation and identification of reaction products are also important factor which leads to the determination of the reaction mechanism.

The intermediate products which are short lived but extremely reactive and free radicals may be formed during the course of the reaction. Free radicals can be demonstrated by the addition of scavengers such as allyl acetate, vinyl monomers and diphenyl picryl hydrazyl which readily combine with the free radicals, Electron paramagnetic resonance (EPR) studies directly give the information about the structure and concentration of free radicals.

Some of the informations about the mechanism of organic and inorganic reactions are obtained also by isotopic and polarographic methods, In the process when one compound is converted into another compound having different oxidation state, the reaction is called redox process. The oxidising and reducing capacity of a compound is often determined by the redox potential from which the knowledge of free energy available for redox reaction. There are several other factors which affect the rate of the chemical reaction. It has been recently established that an increase in electronegativity causes oxidation, the oxidation and reduction reactions are thus complimentary and take place simultaneously. Several redox reagents have been used from time to time overall as well as step by step redox reactions. The most commonly used reagents are permanganate, dichromate, peroxide sulphate, hexacyanoferrate (III), cerium (IV) and vanadium (V).

In the present study we propose to determine the chemical reaction rate with possible variation of parameters. This would give a

clear picture for optimum conditions for maximum output.

Since kinetics is the main feature to determine the rate of reaction in industries by using appropriate catalyst one may control a reaction and may set in a desired path.

Platinic metals (Os, Ir, Ru, Rh etc.) are very important catalysts for the oxidation of various compounds. These catalysts are very important in view of emerging technology.

These catalysts may also be used in biological reactions in living creatures and their physiological studies which may open a view era in genetic engineering and polymer technology.

## A BRIEF SUMMARY OF THE RESULTS OBTAINED

The present thesis deals with the oxidation of ethylene glycol, propylene glycol and buylene glycol in sulphuric acid medium by Ce (IV) using Ru (III) as catalyst.

(I) In each reaction, the reaction is zero order with respect to Ce (IV). Chapter- 3

Ist order in cyclic alcohol with respect to Ce (IV)

(II) Each reaction follows zero order kinetics with respect to (H<sup>+</sup>). Chapter- 5

No effect (Zero order)

(III) In each reaction, the reaction is first order with respect to Ru (III) Chloride. Chapter- 6

Ist order with respect to Ru (III) chloride in cyclic alcohol

(IV) Each reaction follows, first order kinetics with respect to each glycols.

(V) Negligible effect of variation of ionic strength of the medium on the rate of oxidation of glycols was observed. Chapter- 4

Ist order with respect to cyclic alcohol

(V) Negligible effect of variation of ionic strength of the medium on the rate of oxidation of glycols was observed. Chapter- 7

No effect (Zero order)

According to kinetic data the reaction mechanism has been proposed. The rate law equation for oxidation of glycols under experimental conditions in general may be represented as follows :

$$\frac{-d \text{ (Ce (IV))}}{dt} = K_1 \text{ (S)} \quad \text{[ Ru (VIII)]} \dots\dots\dots(1)$$

Since  $\text{[Ru (VIII)]} = \text{[Ru (III)]}$  as earlier reported, hence equation (1) may be written as

$$\frac{-d \text{ (Ce (IV))}}{dt} = K_1 \text{ (S)} \quad \text{[ Ru (III)]} \dots\dots\dots(2)$$

Where 'S' represents the glycols, Since the oxidation of glycols is independent of sulphuric acid concentrations, hence neutral glycol species is involved in the rate determining step.

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## **CHAPTER-II**

### **EXPERIMENTAL**

## 2.1 MATERIALS EMPLOYED :

The samples of Ethylene glycol of B.D.H. Biochemical, Propylene glycol of B.D.H, L.R. glaxo laboratories Ltd. Boday and Butylene glycol of B.D.H. chemicals Ltd. Poole England were used.

Their standard solutions were prepared by dissolving a weighed quantity of the sample in distilled water.

Ceric Sulphate, ferrous ammonium Sulphate, ferroin were all B.D.H. Analar grade chemicals. Sulphuric acid is of A.R. Mark.

Solution of Ceric Sulphate was prepared by warming in Sulphuric acid and water, The strength of Sulphuric acid was maintained at least 0.5 N, that was titrated against ferrous ammonium Sulphate using ferroin as indicator.

Solution of sulphuric acid was made in distilled water and standardised by sodium hydroxide which was standardised by standard solution of oxalic acid.

For ionic strength variation and keeping the ionic strength constant, sodium sulphate was used, Known amount of sodium sulphate was dissolved in distilled water.

Ceric Sulphate of different strengths was used as oxidant and also as titrant.

## 2.2 PROCEDURE :

The progress of the reaction was followed by estimating the amounts of remaining cerium (IV) at different intervals of time. The requisite volumes of standard Ceric Sulphate, Sulphuric Acid and catalyst Ru (III) and water are taken in 50 ml. conical flask which was kept in a thermostat to maintain the desired temperature. Requisite volume of compound solution was taken in another conical flask which was also kept in the same thermostat. After about half an hour when the reactants had attained the temperature of the bath, the reaction was initiated by adding specified amount of compound solution.

The kinetics were followed by removing 5 ml of alcohols after suitable intervals and quenching the reaction by adding it to a known excess of standard Solution of ferrous ammonium sulphate. The remaining excess of ferrous ammonium Sulphate was determined by titrating it against standard solution of Ceric Sulphate using ferroin as indicator. Two drops of ferroin was used in each titration as indicator and its end correction was made in each titre value. The titre value after ferroin correction giving the volume of Cerium (IV) consumed in 5 ml of the reaction mixture and from these values the concentration of remaining Cerium (IV) were calculated at different intervals of time.

The experimental data thus obtained at different intervals of time were utilised first in fixing the order of the reaction with respect to Ce (IV) and there after order with respect to other reactive species is ascertained by usual standard methods.

During preliminary investigations, it has been observed that none of the reactions under investigation here were found to be affected by change in ionic strength of the medium and hence in following chapters experiments have been carried out without maintaining ionic strength of the medium constant.

## **CHAPTER-III**

**DETERMINATION OF ORDER OF REACTION  
WITH RESPECT TO Ce (IV) IN OXIDATION  
OF DIOLS & CYCLIC ALCOHOLS IN  
PRESENCE OF Ru (III) IN ACIDIC MEDIUM**

### 3. Determination of order of reaction with respect to Ce (IV) in oxidation of Glycols and cyclic alcohols in presence of Ru (III) in Acidic Medium

In this chapter an attempt has been made to study the dependence of oxidation of ethylene glycol, propylene glycol, butylene glycol, cyclopentanol and cyclohexanol by ceric sulphate in the presence of Ru (III) chloride in acidic medium an oxidant which is Ce (IV). In order to do so, a number of experiments with varying concentrations of ceric sulphate but at fixed concentrations of all other reactants have been carried out.

In each table  $(-dc/dt)$  values have been recorded. The value of  $(-dc/dt)$  has been calculated by slope of the tangent drawn on the curve obtained on plotting remaining concentration of (Ce (IV)) against time. The concentration of (Ce (IV)), (at which  $(-dc/dt)$  calculated) was also recorded in each table. The results of various experiments obtained in oxidation of, ethylene glycol, propylene glycol and butylene glycol are reported in table 3.1 - 3.7 tables 3.8- 3.14, tables 3.15-3.21 respectively. The results of various experiments obtained in oxidation of cyclopentanol and cyclohexanol are reported in table 3.22-3.36 respectively. The Kinetic data of tables 3.1-3.7, 3.8-3.14, 3.15-3.21 have been summarised in tables 3.22, 3.23, 3.24 respectively. The kinetic data of tables 3.25-3.30, 3.31-3.36 have been summarised in tables 3.37, 3.38 respectively.

TABLE 3.1  
Temperature 35°C

$(\text{Ce (IV)}) = 25.00 \times 10^{-4} \text{ M},$        $(\text{Ethylene Glycol}) = 2.00 \times 10^{-2} \text{ M}$   
 $(\text{H}_2\text{SO}_4) = 0.40 \text{ M},$        $(\text{Ru (III)}) = 0.60 \times 10^{-6} \text{ M}$

Time (min)	ml of Ce $(\text{SO}_4)_2$ ( $1.00 \times 10^{-3} \text{ M}$ )	$(\text{Ce (SO}_4)_2) \times 10^4 \text{ M}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	1.78		
30	1.90		
90	2.00		
150	2.22		
210	2.78	24.50	1.22
270	3.38		
330	4.32		

\* - Conc. of Ceric Sulphate at which  $(-dc/dt)$  was determined.



TABLE 3.2  
Temperature 35°C

(Ce (IV)) = 20.00 X 10 <sup>-4</sup> M,		(Ethylene Glycol) = 2.00 X 10 <sup>-2</sup> M	
(H <sub>2</sub> SO <sub>4</sub> ) = 0.40 M,		(Ru (III)) = 0.60 X 10 <sup>-6</sup> M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (1.00 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.26		
30	4.52		
60	4.60		
90	4.70	19.50	1.28
150	5.22		
210	6.22		
270	6.30		
330	7.32		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.3  
Temperature 35°C

(Ce (IV)) =  $16.70 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.94		
30	6.00		
60	6.50		
90	7.02	16.00	1.30
150	7.48		
210	8.00		
270	8.52		
330	12.58		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.4  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	6.64		
5	7.20		
10	8.22		
20	9.20	9.50	1.28
30	11.20		
40	12.32		
50	13.24		
60	15.02		
70	16.22		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.5  
Temperature 35°C

(Ce (IV)) =  $8.00 \times 10^{-4}$  M,                      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,                                      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.00		
5	3.00		
10	4.00		
15	5.00	7.50	1.24
20	6.25		
25	7.32		
30	8.55		
35	9.60		
40	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.6  
Temperature 35°C

(Ce (IV)) =  $6.60 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	3.32		
5	4.52		
10	5.20		
15	6.20	6.00	1.31
20	7.20		
25	8.22		
30	9.44		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.7  
Temperature 35°C

(Ce (IV))	= 5.00 X 10 <sup>-4</sup> M,	( Ethylene Glycol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.40 M,	(Ru (III))	= 0.60 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
2	5.26		
4	6.02		
6	7.25	4.50	1.25
8	8.26		
10	9.00		
12	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.8  
Temperature 35°C

(Ce (IV)) = 25.00 X 10<sup>-4</sup> M,                      (Propylene Glycol) = 2.00 X 10<sup>-2</sup> M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,                                      (Ru (III)) = 0.20 X 10<sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (1.00 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	1.78		
10	2.62		
40	2.84		
100	3.22	24.50	3.25
160	4.30		
220	4.92		
280	5.30		
340	6.80		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.9  
Temperature 35°C

(Ce (IV)) =  $20.00 \times 10^{-4}$  M, ( Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.28		
10	4.60		
40	5.02		
70	5.12	19.50	3.30
100	5.90		
160	6.30		
190	6.80		
220	7.10		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 3.10  
Temperature 35°C

(Ce (IV)) =  $16.50 \times 10^{-4}$  M,      ( Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.94		
5	6.90		
25	7.40		
55	8.12	16.00	3.36
115	8.34		
145	9.02		
175	9.04		
205	9.60		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.11  
Temperature 35°C

(Ce (IV)) = $12.50 \times 10^{-4}$ M,		( Propylene Glycol) = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> So <sub>4</sub> ) = 0.50 M,		(Ru (III)) = $0.20 \times 10^{-6}$ M	
Time (min)	ml of Ce (So <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.16		
10	5.62		
30	6.24		
50	6.92	12.00	3.30
70	7.24		
90	8.42		
110	9.00		
130	10.62		
150	12.42		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.12  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		[ Propylene Glycol] = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 0.50 M,		[Ru (III)] = $0.20 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	2.21		
10	3.31		
20	4.52	9.50	3.32
30	5.82		
40	9.40		
50	10.22		
60	11.00		
80	12.50		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.13  
Temperature 35°C

(Ce (IV)) =  $6.50 \times 10^{-4}$  M,                      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,                                      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.80		
5	6.20		
10	7.82		
15	8.42	6.00	3.18
20	9.82		
25	10.42		
30	10.92		
35	11.52		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.14  
Temperature 35°C

(Ce (IV)) =  $5.00 \times 10^{-4}$  M, (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	7.41		
2	8.20		
4	9.00		
6	10.22	4.50	3.41
8	10.90		
10	11.02		
12	11.80		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.15  
Temperature 35°C

(Ce (IV)) = 25.00 X 10<sup>-4</sup> M,                      ( Butylene Glycol) = 2.00 X 10<sup>-2</sup>M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,                                      (Ru (III)) = 0.20 X 10<sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	1.78		
5	3.82		
15	6.22		
25	8.42	24.50	3.12
35	9.90		
45	11.00		
55	11.82		
75	13.00		
85	14.10		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.16  
Temperature 35°C

(Ce (IV)) = 20.00 X 10<sup>-4</sup> M,                      ( Butylene Glycol) = 2.00 X 10<sup>-2</sup>M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,                                      (Ru (III)) = 0.20 X 10<sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (1.00 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.28		
5	5.42		
15	6.82		
25	8.54	19.50	3.06
35	9.24		
45	10.00		
55	11.54		
75	12.42		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.17  
Temperature 35°C

(Ce (IV)) =  $16.50 \times 10^{-4}$  M,      ( Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.94		
5	6.80		
10	8.20		
20	9.52	16.00	3.18
30	10.02		
40	11.82		
60	12.42		
80	13.32		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 3.18  
Temperature 35°C

(Ce (IV))	= 12.50 X 10 <sup>-4</sup> M,	( Butylene Glycol) = 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III)) = 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.15		
10	6.22		
20	7.80		
30	9.22	12.00	3.36
40	11.25		
50	12.90		
60	14.62		
70	16.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.19  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      ( Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
10	4.22		
30	6.52		
40	7.74	9.50	3.32
50	8.34		
60	8.92		
70	9.60		
80	10.02		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.20  
Temperature 35°C

(Ce (IV)) =  $8.00 \times 10^{-4}$  M,      ( Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>So<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (So <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.40		
10	5.00		
20	5.62		
30	6.24	7.50	3.25
40	8.00		
50	9.24		
60	9.02		
70	11.02		
80	12.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.21  
Temperature 35°C

(Ce (IV))	= 5.00 X 10 <sup>-4</sup> M,	( Butylene Glycol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> So <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (So <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	7.40		
5	7.95		
15	8.00		
25	8.60	4.50	3.34
45	9.00		
65	9.80		
85	9.28		
105	11.50		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 3.22

(Ethylene Glycol) =  $2.00 \times 10^{-2} \text{M}$ ,  
 (Ru (III)) =  $0.60 \times 10^{-6} \text{M}$ ,  
 ( $\text{H}_2\text{SO}_4$ ) =  $0.40 \text{M}$   
 Temperature  $35^\circ\text{C}$

Ce (IV) $\times 10^{-4} \text{M}$	Ce (IV) $\times 10 \times 10^{-4} \text{M}$	$(-dc/dt) \times 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$
5.00	4.50	1.25
6.50	6.00	1.31
8.00	7.50	1.24
10.00	9.50	1.28
16.50	16.00	1.30
20.00	19.50	1.28
25.00	24.50	1.22

TABLE 3.23

( Propylene Glycol) = $2.00 \times 10^{-2} \text{M}$ , (Ru (III)) = $0.20 \times 10^{-6} \text{M}$ ,		( $\text{H}_2\text{SO}_4$ ) = $0.50 \text{M}$ Temperature $35^\circ\text{C}$
Ce (IV) $\times 10^{-4} \text{M}$	Ce (IV) $\times 10 \times 10^{-4} \text{M}$	$(-dc/dt) \times 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$
5.00	4.50	3.40
6.50	6.00	3.18
10.00	9.50	3.32
12.50	12.00	3.30
16.50	16.00	3.36
20.00	19.50	3.30
25.00	24.50	3.25

TABLE 3.24

( Butylene Glycol) =  $2.00 \times 10^{-2} \text{M}$ ,  
 (Ru (III)) =  $0.02 \times 10^{-6} \text{M}$ ,  
 ( $\text{H}_2\text{SO}_4$ ) =  $3.00 \text{M}$   
 Temperature  $35^\circ\text{C}$

Ce (IV) $\times 10^{-4} \text{M}$	Ce (IV) $\times 10 \times 10^{-4} \text{M}$	$(-dc/dt) \times 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$
5.00	4.50	3.34
8.00	7.50	3.25
10.00	9.50	3.32
12.50	12.00	3.36
16.50	16.00	3.18
20.00	19.50	3.06
25.00	24.50	3.11

A close examination of data of tables 3.22- 3.24 clearly indicates that  $(-dc/dt)$  values in each of above tables are nearly constant, showing zero order dependence on Ce (IV).

TABLE 3.25  
Temperature 35°C

(Ce (IV)) =  $16.50 \times 10^{-4}$  M, (Cyclopentanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M  
 (Ce (SO<sub>4</sub>)<sub>2</sub>)  $10^4$  M = 16.00

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.96	
5	6.92	
25	7.40	
45	8.12	3.40
65	8.30	
85	9.04	
110	9.09	
140	9.40	
170	9.62	



TABLE 3.26  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	( Cyp)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> So <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M
(Ce (SO <sub>4</sub> ) <sub>2</sub> )	10 <sup>4</sup> M = 9.50		

Time (min)	ml of Ce (So <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48	
5	3.22	
25	3.32	
45	4.48	3.33
65	5.82	
85	9.42	
110	10.22	
140	11.00	
170	12.44	

TABLE 3.27  
Temperature 35°C

$(\text{Ce (IV)})$	$= 8.50 \times 10^{-4} \text{ M,}$	$(\text{Cyp})$	$= 2.00 \times 10^{-2} \text{ M}$
$(\text{H}_2\text{SO}_4)$	$= 0.50 \text{ M,}$	$(\text{Ru (III)})$	$= 0.20 \times 10^{-6} \text{ M}$
$(\text{Ce (SO}_4)_2)$	$10^4 \text{ M} = 8.00$		

Time (min)	ml of $\text{Ce (SO}_4)_2$ ( $0.50 \times 10^{-3} \text{ M}$ )	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	2.44	
5	3.18	
25	3.28	
45	4.50	3.28
65	5.78	
85	9.00	
110	10.20	
140	11.00	
170	12.22	

TABLE 3.28  
Temperature 35°C

(Ce (IV))	= $6.50 \times 10^{-4}$ M,	(Cyp)	= $2.00 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= $0.20 \times 10^{-6}$ M
(Ce (SO <sub>4</sub> ) <sub>2</sub> )	$10^4$ M = 6.00		

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	5.74	
5	6.26	
25	7.80	
45	8.44	3.16
65	9.84	
85	10.44	
110	10.94	
140	11.20	
170	11.40	

TABLE 3.29  
Temperature 35°C

$(\text{Ce (IV)}) = 4.50 \times 10^{-4} \text{ M},$                        $(\text{Cyp}) = 2.00 \times 10^{-2} \text{ M}$   
 $(\text{H}_2\text{SO}_4) = 0.50 \text{ M},$                                  $(\text{Ru (III)}) = 0.20 \times 10^{-6} \text{ M}$   
 $(\text{Ce (SO}_4)_2) 10^4 \text{ M} = 4.00$

Time (min)	ml of $\text{Ce (SO}_4)_2$ ( $0.50 \times 10^{-3} \text{ M}$ )	$(-\text{dc}/\text{dt}) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	5.76	
5	6.28	
25	7.82	
45	8.46	3.14
65	9.80	
85	10.40	
110	10.92	
140	11.22	
170	11.30	

TABLE 3.30  
Temperature 35°C

(Ce (IV))	= $2.50 \times 10^{-4}$ M,	(Cyp)	= $2.00 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= $0.20 \times 10^{-6}$ M
(Ce (SO <sub>4</sub> ) <sub>2</sub> )	$10^4$ M = 2.00		

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.98	
5	5.10	
25	6.44	
45	7.58	3.10
65	8.02	
85	10.00	
110	11.20	
140	11.43	

TABLE 3.31  
Temperature 35°C

[Ce (IV)]	= 12.50 X 10 <sup>-4</sup> M,	[Cyclohexanol]	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M
[Ce (SO <sub>4</sub> ) <sub>2</sub> ]	10 <sup>4</sup> M = 12.00		

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.14	
15	6.22	
30	7.80	
45	9.26	3.38
60	11.22	
75	12.92	
90	14.60	
105	15.98	

TABLE 3.32  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M  
 (Ce (SO<sub>4</sub>)<sub>2</sub>)  $10^4$  M = 9.50

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48	
15	4.18	
30	6.55	
45	7.74	3.33
60	8.30	
75	8.94	
90	9.62	
105	10.00	

TABLE 3.33  
Temperature 35°C

$[\text{Ce (IV)}] = 8.00 \times 10^{-4} \text{ M},$                        $[\text{Cyclohexanol}] = 2.00 \times 10^{-2} \text{ M}$   
 $[\text{H}_2\text{SO}_4] = 3.00 \text{ M},$                                        $[\text{Ru (III)}] = 0.20 \times 10^{-6} \text{ M}$   
 $[\text{Ce (SO}_4)_2] 10^4 \text{ M} = 7.50$

Time (min)	ml of $\text{Ce (SO}_4)_2$ ( $0.50 \times 10^{-3} \text{ M}$ )	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	4.38	
15	4.98	
30	5.64	
45	6.26	3.26
60	7.98	
75	9.28	
90	9.84	
105	11.00	



TABLE 3.34  
Temperature 35°C

(Ce (IV)) =  $6.00 \times 10^{-4}$  M,                      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,                                      (Ru (III)) =  $0.02 \times 10^{-6}$  M  
 (Ce (SO<sub>4</sub>)<sub>2</sub>)  $10^4$  M = 5.50

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	4.32	
15	4.94	
30	5.66	
45	6.28	3.20
60	7.98	
75	9.40	
90	9.78	
105	10.02	

TABLE 3.35  
Temperature 35°C

(Ce (IV)) =  $4.50 \times 10^{-4}$  M, (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M, (Ru (III)) =  $0.02 \times 10^{-6}$  M  
 (Ce (SO<sub>4</sub>)<sub>2</sub>)  $10^4$  M = 4.00

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	3.98	
15	4.44	
30	5.90	
45	5.98	3.17
60	6.70	
75	7.40	
90	8.30	
105	9.40	

TABLE 3.36  
Temperature 35°C

$[\text{Ce (IV)}] = 2.50 \times 10^{-4} \text{ M},$                        $[\text{Cyclohexanol}] = 2.00 \times 10^{-2} \text{ M}$   
 $[\text{H}_2\text{SO}_4] = 3.00 \text{ M},$                                $[\text{Ru (III)}] = 0.02 \times 10^{-6} \text{ M}$   
 $[\text{Ce (SO}_4)_2] 10^4 \text{ M} = 2.00$

Time (min)	ml of $\text{Ce (SO}_4)_2$ ( $0.50 \times 10^{-3} \text{ M}$ )	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	3.44	
15	4.98	
30	5.99	
45	5.40	3.13
60	6.74	
75	7.00	
90	8.20	
105	9.66	

TABLE 3.37  
Temperature 35°C

(Cyclopentanol) =  $2.00 \times 10^{-2} \text{M}$       (Ru (III)) =  $0.20 \times 10^{-6} \text{M}$   
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M

Ce (IV) X 10 <sup>-4</sup> M	Ce (IV) X 10 X 10 <sup>4</sup> M	(-dc/dt) X 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
2.50	2.00	3.10
4.50	4.00	3.14
6.50	6.00	3.16
8.50	8.00	3.28
10.00	9.50	3.33
16.50	16.00	3.40

TABLE 3.38  
Temperature 35°C

(Cyclohexanol) =  $2.00 \times 10^{-2} \text{ M}$       (Ru (III)) =  $0.20 \times 10^{-6} \text{ M}$   
 $(\text{H}_2\text{SO}_4)$  = 3.00 M

Ce (IV) X $10^{-4} \text{ M}$	Ce (IV) X $10 \times 10^4 \text{ M}$	$(-dc/dt) \times 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
2.50	2.00	3.13
4.50	4.00	3.17
6.00	5.50	3.20
8.00	7.50	3.26
10.00	9.50	3.33
12.50	12.00	3.38

It is evident from the data of tables 3.37 and 3.38 that the values of  $-dc/dt$  increases linearly with the increase in concentration of each, of the cyclo alcohol. So it indicates first- order dependence of the reactions on each cyclo alcohol.

## **CHAPTER -IV**

**DETERMINATION OF ORDER OF REACTION  
WITH RESPECT TO DIOLS & CYCLIC  
ALCOHOLS IN THEIR OXIDATION BY Ce (IV) IN  
PRESENCE OF Ru (III) IN ACIDIC MEDIUM**

#### 4. DETERMINATION OF ORDER OF REACTION WITH RESPECT TO DIOLS & CYCLIC ALCOHOLS IN THEIR OXIDATION BY $Ce(IV)$ IN PRESENCE OF $Ru(III)$ IN ACIDIC MEDIUM

This Chapter deals with the study of determination of order of the reaction with respect to each of cyclopentanol and cyclohexanol, ethylene glycol, propylene glycol butylene glycol used as reducing agent in the reaction involving  $Ce(IV)$  and  $Ru(III)$  as oxidant and catalyst and respectively in acidic medium. Here a set of experiments with each glycols have been performed at different concentrations of aforesaid glycols, but at fixed concentrations of all other reactants at  $35^{\circ}C$ . The results of the various experiments are reported here in tables 4.1-4.6, tables 4.7-4.12 tables 4.13-4.18 in oxidation of ethylene glycol, propylene glycol and butylene glycol respectively. The results of experiments of oxidation of cyclopentanol, cyclohexanol has been given in tables. 4.22-4.27 and 4.28-4.33.

The kinetic observations of tables 4.1-4.6, 4.7-4.12, 4.13-4.18 have been summarised in tables. 4.19, 4.20, 4.21 respectively. The kinetic observations of tables 4.22-4.27, 4.28-4.33 have been summarised in tables 4.34, 4.35 respectively.

TABL  
Temperati

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ethylene Glycol) =  $10.00 \times 10^{-2}$  M  
 ( $H_2SO_4$ ) = 0.40 M, (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce ( $SO_4$ ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce ( $SO_4$ ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	4.30		
4	7.30		
6	8.22	9.50	12.48
8	9.48		
10	10.92		
12	11.85		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 4.2  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $5.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	3.20		
4	4.80		
6	5.20	9.50	6.38
10	6.20		
15	7.50		
20	8.24		
30	9.46		
40	11.54		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.3  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $4.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
10	4.00		
20	5.00		
30	6.00	9.50	5.02
40	7.52		
50	8.32		
60	9.20		
70	10.18		
80	12.42		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.4  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $3.33 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
30	4.00		
60	5.00		
90	6.24	9.50	4.01
120	7.24		
150	8.00		
180	9.24		
210	10.86		
240	12.20		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.5  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.50 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M.	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.41		
60	3.90		
120	5.00		
180	6.62	9.50	3.14
240	8.62		
300	9.80		
360	10.51		
420	11.50		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.6  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		(Ethylene Glycol) = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 0.40 M,		(Ru (III)) = $0.12 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.40		
60	3.00		
120	3.82		
180	4.50	9.48	2.52
240	5.00		
300	5.72		
360	6.12		
420	8.50		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.7  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $5.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	3.40		
4	5.10		
6	6.84	9.48	5.14
8	7.94		
10	8.84		
12	9.44		
14	10.46		
16	11.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.8  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $3.33 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	5.26		
10	6.26		
15	7.24	9.50	3.40
20	8.80		
25	9.22		
30	10.00		
35	10.98		
40	11.40		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.9  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Propylene Glycol)= $2.50 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III)) = $0.12 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.40		
10	4.00		
20	5.10	9.42	2.60
30	6.24		
40	7.26		
50	9.32		
60	11.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 4.10  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Propylene Glycol)= 2.00 X 10 <sup>-2</sup> M	
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.12 X 10 <sup>-6</sup> M
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.60		
10	3.00		
20	4.00		
30	5.60	9.50	2.02
40	6.80		
70	8.22		
100	9.64		
130	11.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.11  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $1.25 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
10	3.00		
30	4.02		
90	5.60	9.50	1.26
150	6.00		
210	7.22		
270	8.00		
330	8.90		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.12  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $1.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.00		
10	2.50		
40	2.80		
70	3.20	9.50	1.00
130	4.20		
190	5.20		
250	5.94		
310	6.92		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.13  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $5.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	4.32		
10	5.10		
20	6.02	9.50	8.22
30	6.82		
40	7.80		
60	8.20		
80	10.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.14  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $3.33 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.62		
5	3.02		
10	4.30		
20	5.12	9.50	5.58
30	6.22		
40	7.30		
50	8.00		
60	9.40		
80	10.02		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.15  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.50 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.54		
5	3.92		
10	4.92		
20	5.82	9.50	4.06
30	6.20		
40	7.24		
50	8.00		
60	9.24		
80	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.16  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		(Butylene Glycol) = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 3.00 M,		(Ru (III)) = $0.02 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.20		
10	4.00		
20	5.60	9.50	3.32
30	6.62		
40	7.22		
50	8.24		
60	9.24		
80	10.40		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.17  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $1.25 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/df) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.54		
5	3.12		
10	4.02		
20	5.24	9.50	2.10
30	6.00		
40	7.32		
50	8.20		
60	9.24		
80	10.24		

\*- Conc. of Ceric Sulphate at which (-dc/df) was determined.



TABLE 4.18  
Temperature 35°C

[Ce (IV)] =  $10.00 \times 10^{-4}$  M, (Butylene Glycol) =  $1.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M, (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.36		
5	3.20		
10	4.70		
20	6.62	9.50	1.71
30	8.22		
40	9.02		
50	9.74		
60	10.34		
80	11.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.19  
Temperature 35°C

$[\text{Ce (IV)}] = 10.00 \times 10^{-4} \text{ M,}$ $[\text{Ru (III)}] = 0.12 \times 10^{-6} \text{ M}$		$[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$
$(\text{Butylene Glycol}) 10^2 \text{ M}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$	$10^5 K_1 = (dc/dt)$ $\text{Sec}^{-1} (\text{Ethylene Glycol})$
2.00	2.52	1.27
2.50	3.14	1.26
3.33	4.01	1.21
4.00	5.02	1.26
5.00	6.38	1.27
10.00	12.48	1.24
<p style="text-align: center;">Average value of <math>K_1 = 1.25 \times 10^{-5} \text{ Sec}^{-1}</math></p>		

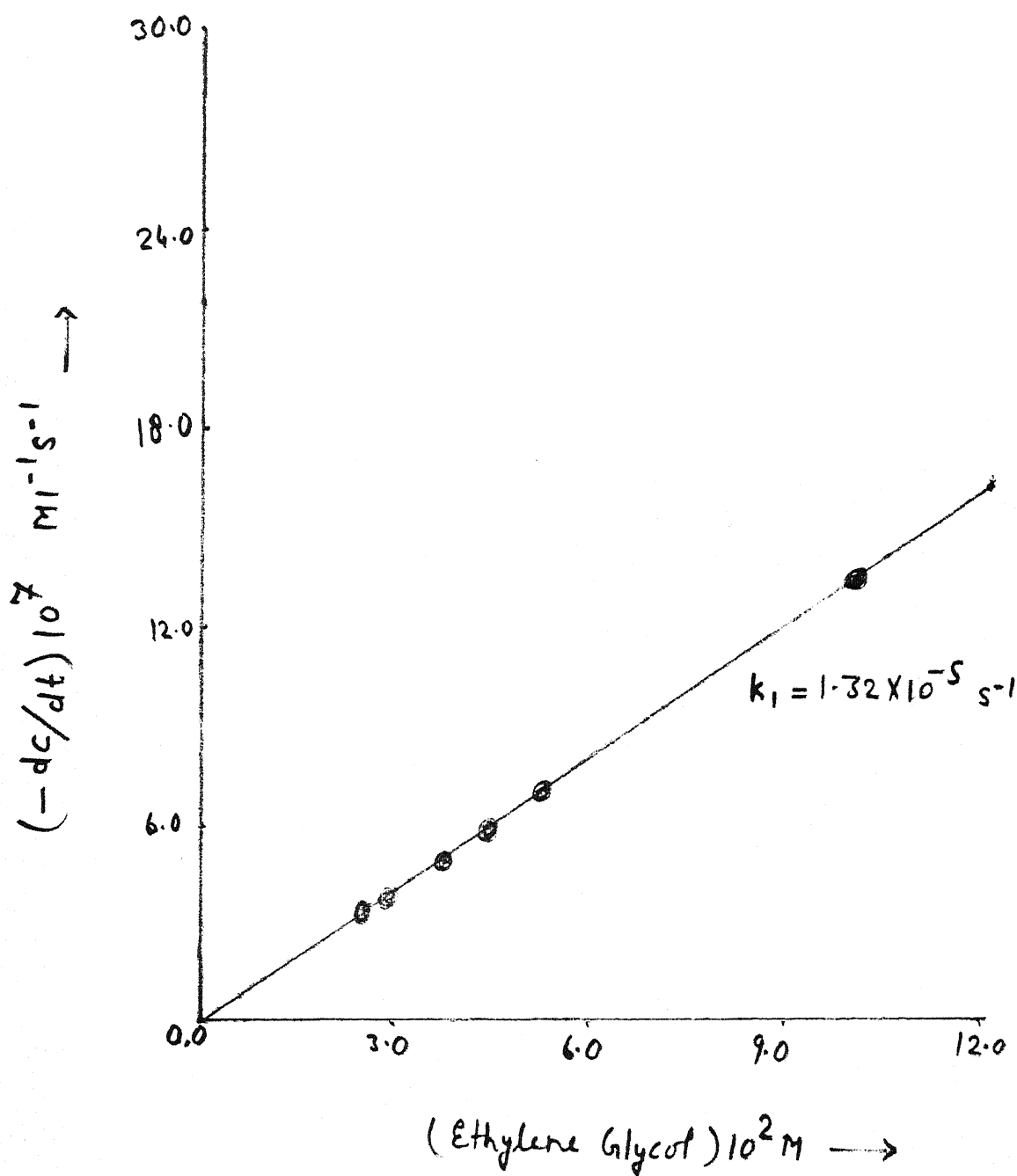


Fig. 4.1

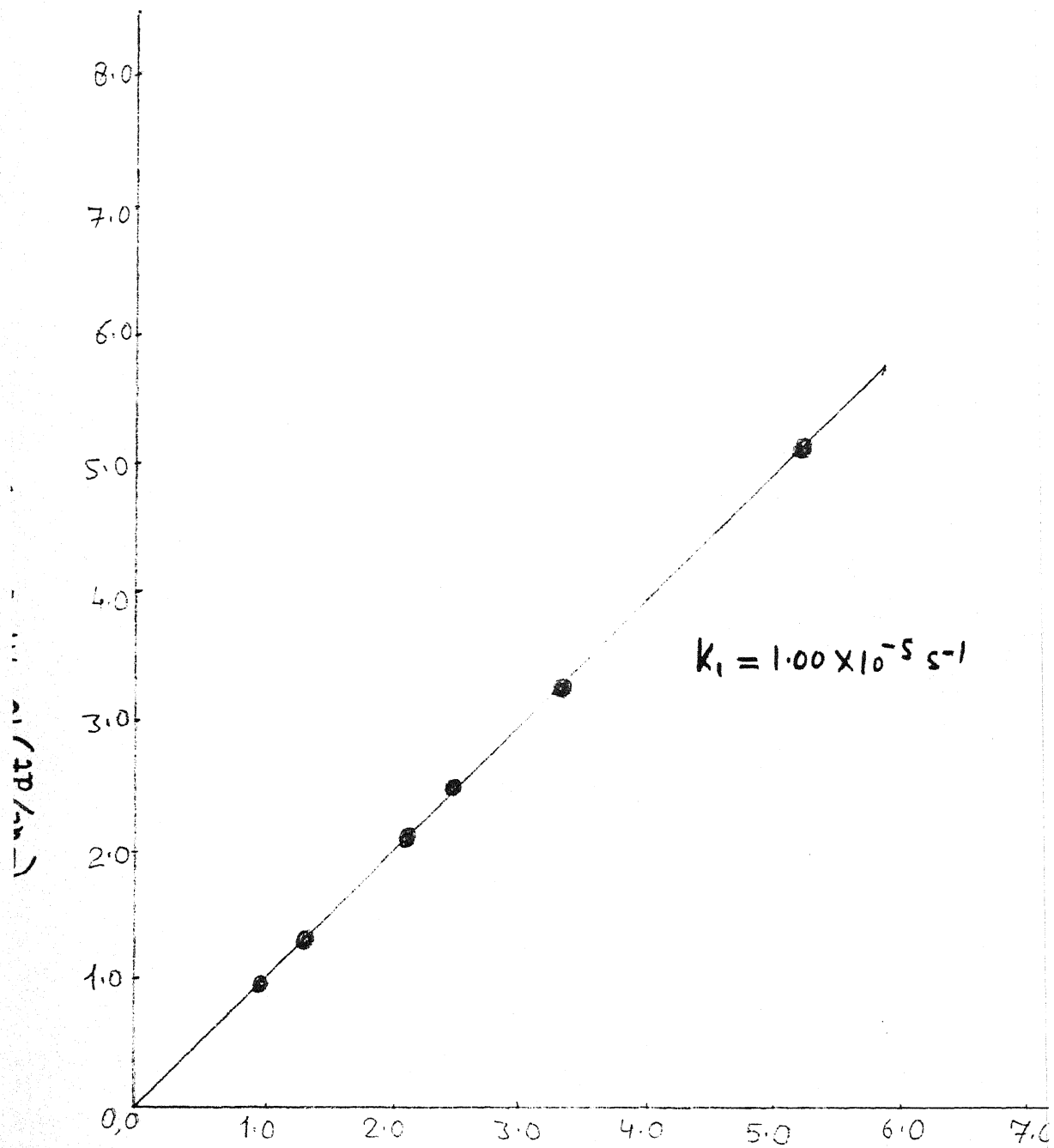
$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$  ,  $[\text{H}_2\text{SO}_4] = 0.40 \text{ M}$   
 $[\text{Ru(III)}] = 0.12 \times 10^{-6} \text{ M}$  , temp.  $35^\circ \text{C}$

TABLE 4.20  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (H<sub>2</sub>So<sub>4</sub>) = 0.50 M  
(Ru (III)) =  $0.12 \times 10^{-6}$  M

(Propylene Glycol) $\times 10^2$ M	$(-dc/dt) 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>	$10^5 K_1 = (dc/dt)$ Sec <sup>-1</sup> (Propylene Glycol)
1.00	1.00	1.00
1.25	1.26	1.02
2.00	2.02	1.02
2.50	2.60	1.04
3.33	3.40	1.02
5.00	5.14	1.03

Average value of  $K_1 = 1.02 \times 10^{-5} \text{Sec}^{-1}$



(Propylene glycol)  $10^2$  M  $\rightarrow$

Fig. 4.2

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$  ,  $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$

$[\text{Ru(III)}] = 0.12 \times 10^{-6} \text{ M}$  , temp. =  $35^\circ\text{C}$

TABLE 4.21  
Temperature 35°C

[Ce (IV)] =  $10.00 \times 10^{-4}$  M,                      (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M  
[Ru (III)] =  $0.02 \times 10^{-6}$  M

(Butylene Glycol) $\times 10^2$ M	$(-dc/dt) \times 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>	$10^5 K_1 = (dc/dt)$ Sec <sup>-1</sup> (Butylene Glycol)
1.00	1.71	1.70
1.25	2.10	1.67
2.00	3.32	1.66
2.50	4.06	1.62
3.33	5.58	1.65
5.00	8.22	1.62
Average value of $K_1 = 1.65 \times 10^{-5}$ Sec <sup>-1</sup>		

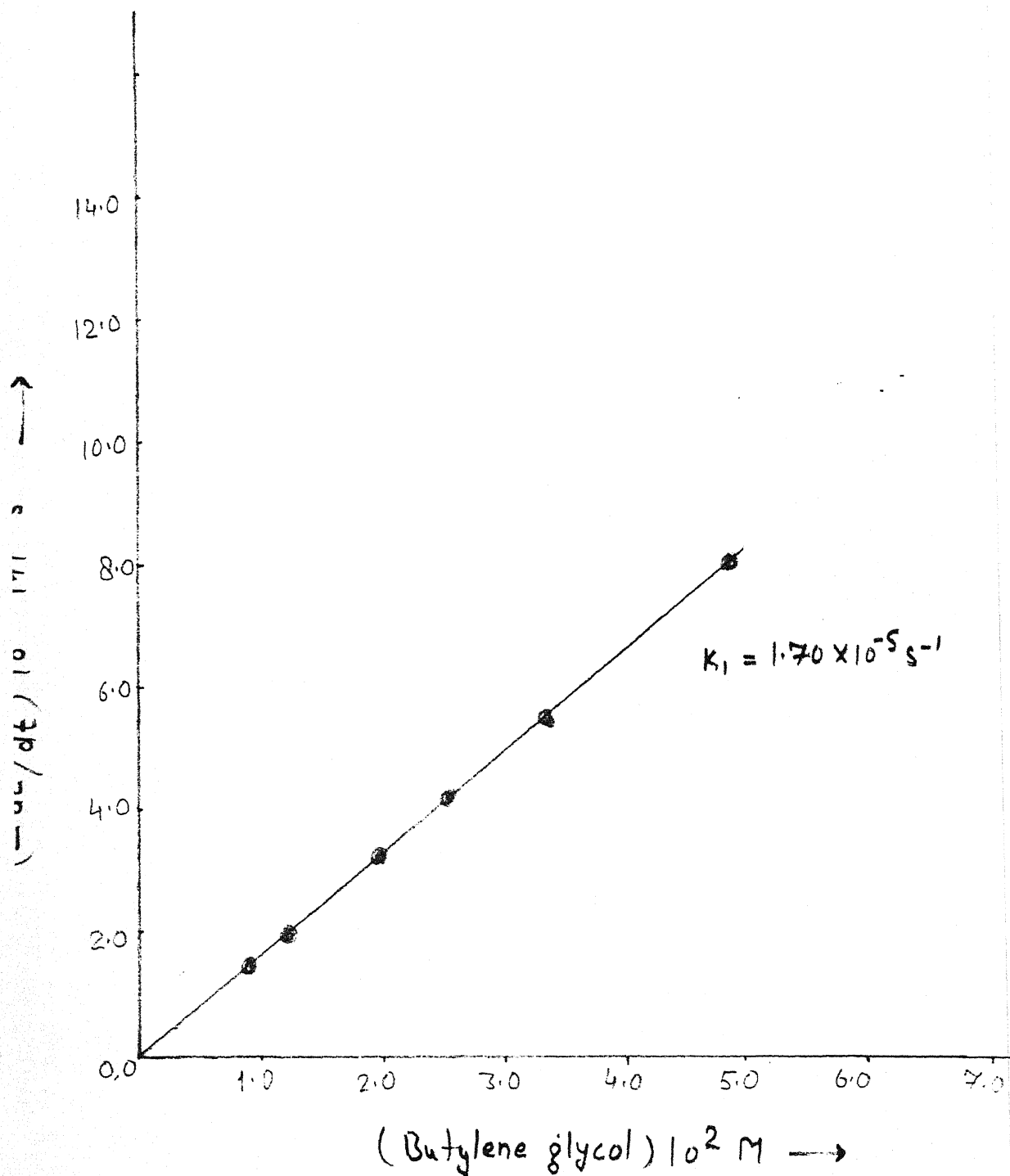


Fig. 4.3

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$  ,  $[\text{H}_2\text{SO}_4] = 3.00 \text{ M}$

$[\text{Ru(III)}] = 0.02 \times 10^{-6} \text{ M}$  ,  $\text{temp.} = 35^\circ\text{C}$

TABLE 4.22  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclopentanol)	= 5.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.12 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.49		
5	3.41		
10	5.10		
15	6.82	9.47	5.15
20	7.94		
30	8.84		
40	9.43		
50	10.44		
60	11.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 4.23  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cypen)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.12 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.51		
5	5.24		
10	6.28		
20	7.23	9.50	3.41
30	8.80		
40	9.22		
50	10.01		
60	10.99		
70	11.40		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.24  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Cypen)	= $2.50 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= $0.12 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
10	3.42		
20	4.02		
30	5.08	9.42	2.62
40	6.22		
70	7.28		
100	9.30		
130	10.98		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.25  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Cypen) =  $2.50 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.62		
10	3.00		
20	4.02		
30	5.50	9.50	2.02
40	6.82		
70	8.24		
100	9.62		
130	11.22		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.26  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cypen)	= 1.25 X 10 <sup>-2</sup> M
(H <sub>2</sub> So <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.12 X 10 <sup>-6</sup> M
Time (min)	ml of Ce (So <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
10	3.02		
30	4.00		
90	5.62	9.50	1.26
150	6.00		
210	7.20		
270	8.02		
330	8.94		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.27  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		(Cypen) = $1.20 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 0.50 M,		(Ru (III)) = $0.12 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.00		
10	2.52		
40	2.82		
70	3.16	9.50	1.00
130	4.22		
190	5.20		
250	5.92		
310	6.92		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.28  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 5.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	4.30		
10	5.10		
20	6.00	9.50	8.20
30	6.80		
40	7.80		
60	8.20		
80	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.29  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $3.32 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.62		
5	3.02		
10	4.32		
20	5.10	9.50	5.56
30	6.20		
40	7.32		
50	8.02		
60	9.44		
80	10.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.30  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 2.50 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.90		
10	4.90		
20	5.80	9.50	4.05
30	6.22		
40	7.22		
50	8.02		
60	9.20		
80	10.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 4.31  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.22		
10	4.02		
20	5.62	9.50	3.34
30	6.60		
40	7.20		
50	8.22		
60	9.22		
80	10.42		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.32  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Cyclohexanol)	= $1.22 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= $0.02 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.10		
10	4.04		
20	5.22	9.50	2.10
30	6.02		
40	7.32		
50	8.16		
60	9.22		
80	10.22		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.33  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 1.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.36		
5	3.22		
10	4.68		
20	6.62	9.50	1.72
30	8.22		
40	9.00		
50	9.72		
60	10.32		
80	11.26		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 4.34  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ru (III)) =  $0.12 \times 10^{-6}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,

(Cyclopentanol) $\times 10^2$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
1.20	1.00
1.25	1.26
2.00	2.02
2.50	2.62
2.00	3.41
5.00	5.15

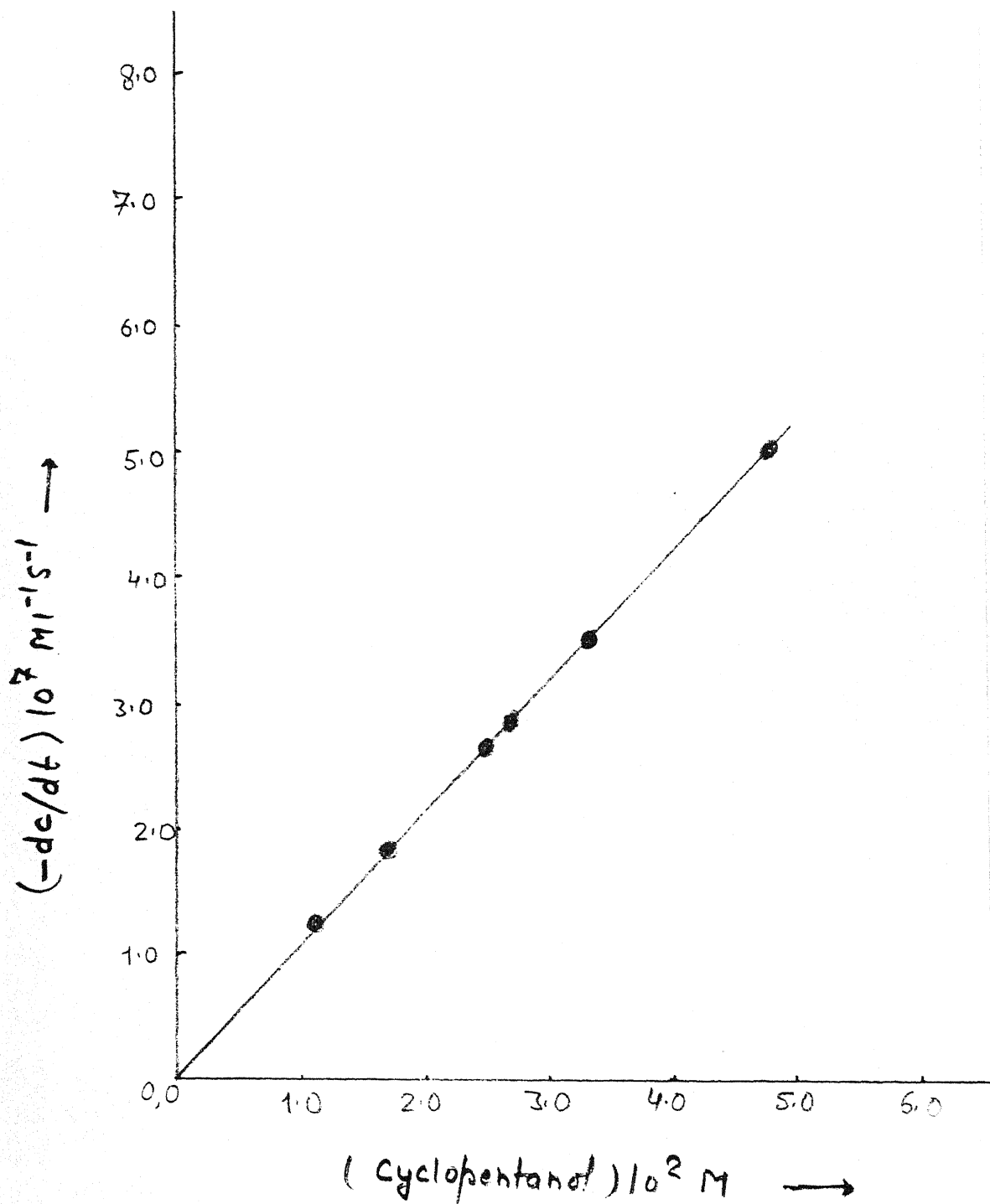


Fig. 4.4

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$  ,  $[\text{R}_4(\text{III})] = 0.12 \times 10^{-6} \text{ M}$   
 $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$  ,  $\text{temp.} = 35^\circ \text{C}$

TABLE 4.35  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ru (III)) =  $0.02 \times 10^{-6}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,

(Cyclohexanol)	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
1.00 X 10 <sup>-2</sup> M	1.72
1.22 X 10 <sup>-2</sup> M	2.10
2.00 X 10 <sup>-2</sup> M	3.34
2.50 X 10 <sup>-2</sup> M	4.05
3.32 X 10 <sup>-2</sup> M	5.56
5.00 X 10 <sup>-2</sup> M	8.20

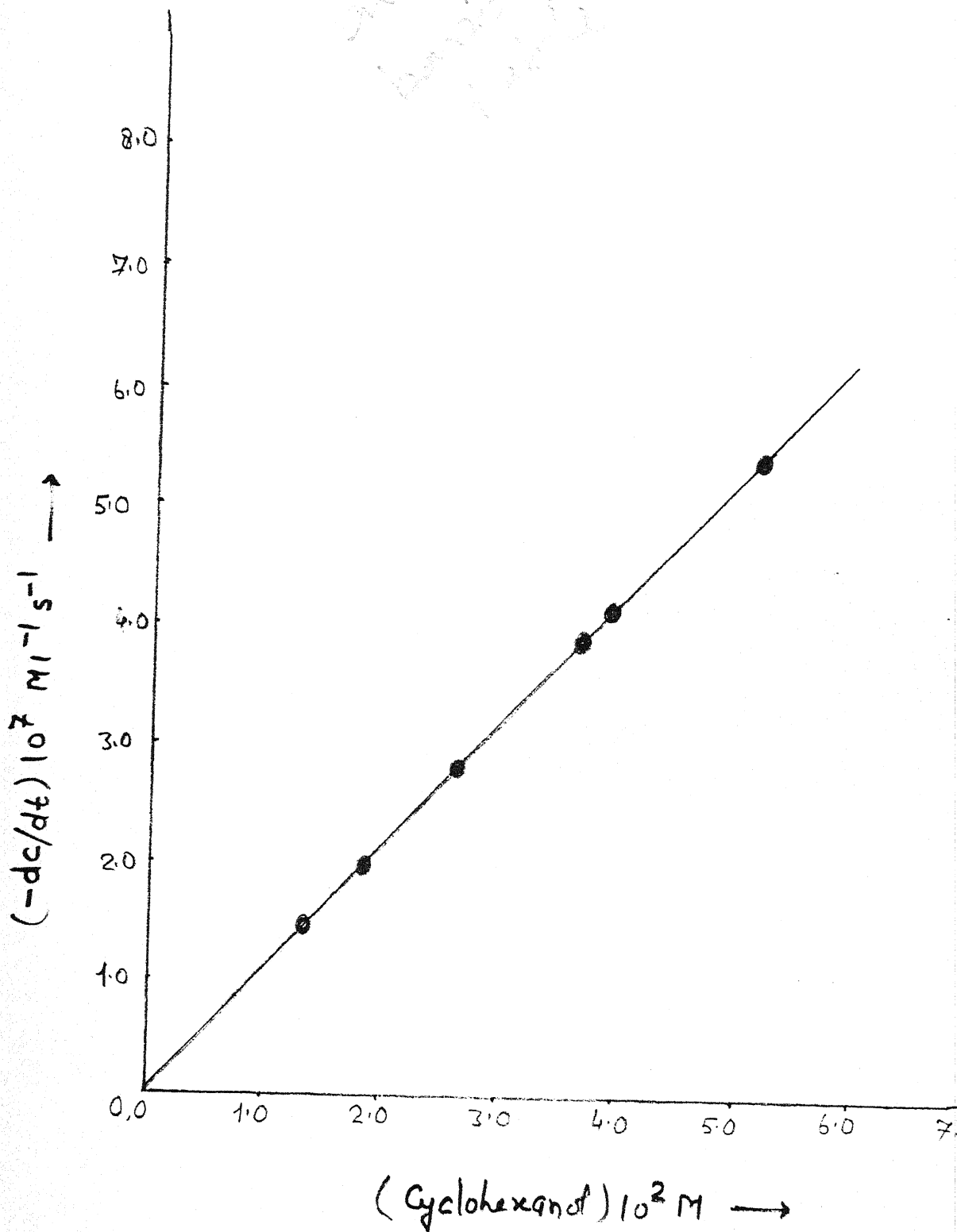


Fig. 4.5

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$ ,  $[\text{Ru(III)}] = 0.02 \times 10^{-6} \text{ M}$   
 $[\text{H}_2\text{SO}_4] = 3.00 \text{ M}$ , temp. =  $35^\circ \text{C}$

It is evident from the data of summarised tables 4.19 - 4.21 and 4.34-4.35 that the values of  $(-dc/dt)$  increase linearly with the increase in concentration of each of the glycol and cycloalcohol used here, indicating first order dependence of the reactions on each glycol and cycloalcohol. This observation here, further, been confirmed graphically by plotting  $(-dc/dt)$  values against (Glycol).

A straight line is obtained in oxidation of each of, ethylene glycol (Fig 4.1), Propylene glycol (Fig 4.2) butylene glycol (Fig 4.3) cyclopentanol (Fig 4.3) cyclohexanol (Fig 4.5). The slopes of the curves give first order rate constant i.e. values in each case. This confirms first order of the various reaction with respect to each glycols and cycloalcohols.



## **CHAPTER -V**

**DETERMINATION OF ORDER OF REACTION  
WITH RESPECT TO SULPHURIC ACID IN Ru (III)  
CATALYSED OXIDATION OF DIOLS & CYCLIC  
ALCOHOL BY Ce (IV)**

## 5- DETERMINATION OF ORDER OF REACTION WITH RESPECT TO SULPHURIC ACID IN Ru (III) CATALYSED OXIDATION OF DIOLS & CYCLIC ALCOHOL BY Ce (IV)

The present chapter deals with study of reactions involving Ce (IV) as oxidant in oxidation of ethylene glycol, Propylene glycol, butylene glycol, cyclopentanol and cyclohexanol in presence of Ru (III) as catalyst with respect to sulphuric acid. The reactions have been studied at different concentrations of sulphuric acid, keeping concentrations of other reactions constant at 35°C. The results obtained in oxidation of ethylene glycol, propylene glycol, butylene glycol, cyclopentanol and cyclohexanol have been recorded in tables 5.7-5.12, 5.13-5.19, 5.23-5.28, 5.29-5.34 respectively. The kinetic data have been summarised in tables. 5.20, 5.21, 5.22, 5.35, 5.36.

TABLE 5.1  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.25 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.00		
10	3.02		
20	3.15	9.50	1.22
30	3.58		
40	4.00		
60	4.12		
90	4.20		
150	4.54		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.2  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		(Ethylene Glycol) = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 0.40 M,		(Ru (III)) = $0.60 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.56		
10	3.00		
20	4.10		
30	5.10	9.50	1.25
50	6.24		
70	7.90		
90	10.20		
120	12.20		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.3  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.55		
5	3.21		
10	4.00		
20	5.00	9.50	1.26
30	6.82		
40	7.22		
50	8.20		
60	10.61		
70	11.62		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.4  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M,		(Ethylene Glycol) = $2.00 \times 10^{-2}$ M	
(H <sub>2</sub> SO <sub>4</sub> ) = 1.00 M,		(Ru (III)) = $0.60 \times 10^{-6}$ M	
Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.31		
10	4.10		
15	5.25	9.50	1.28
20	6.24		
25	7.80		
30	10.22		
35	11.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.5  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 1.25 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
2	3.80		
4	4.02		
6	5.22	9.50	1.20
8	6.41		
10	7.60		
15	8.26		
20	9.64		
25	11.22		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.6  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 1.50 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.56		
2	3.42		
4	4.10		
6	5.40	9.48	1.30
8	6.22		
10	8.32		
12	9.22		
14	11.20		
16	12.20		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 5.7  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.20 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
10	3.00		
30	3.60		
60	4.02	9.50	3.26
90	4.80		
120	5.62		
150	6.02		
180	7.26		
210	8.84		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.8  
Temperature 35°C

[Ce (IV)] =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.30 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
10	3.00		
30	4.90		
50	5.22	9.48	3.36
70	6.90		
90	7.32		
110	8.42		
130	9.90		
150	10.40		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.9  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.00		
10	3.90		
20	4.64	9.50	3.32
40	6.00		
60	7.10		
80	8.22		
100	9.40		
120	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.10  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.20		
10	4.80		
20	5.84	9.50	3.31
40	7.44		
60	9.42		
80	11.44		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.11  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.70 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.12		
10	4.24		
15	5.24	9.50	3.40
20	6.00		
25	7.20		
30	9.86		
40	10.00		
50	11.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.12  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 1.00 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
2	3.42		
4	5.56		
6	6.62	9.50	3.20
10	8.42		
14	9.02		
18	10.42		
22	11.06		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.13  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	5.10		
10	7.20		
15	9.00	9.50	3.35
20	9.70		
25	10.00		
30	11.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.14  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.49		
5	3.23		
10	5.99		
15	7.53	9.50	3.26
20	9.62		
25	10.00		
30	10.98		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 5.15  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 1.00 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	4.90		
10	6.90		
15	8.50	9.50	3.50
20	9.20		
25	10.00		
30	11.08		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.16  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 1.50 M, (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.46		
5	3.52		
10	5.52		
15	6.82	9.50	3.08
20	7.81		
25	8.80		
30	9.02		
40	9.82		
50	10.90		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.17  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 2.00 M, (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.66		
10	4.34		
15	5.40	9.50	3.22
20	6.10		
25	7.40		
30	8.30		
40	9.52		
50	10.90		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.18  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Butylene Glycol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 2.50 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.54		
5	4.10		
10	5.80		
15	7.10	9.50	3.40
20	8.10		
25	8.70		
35	9.70		
45	10.00		
65	11.20		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.19  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.62		
10	4.60		
15	5.50		
20	6.32	9.50	3.33
30	7.42		
40	8.28		
60	9.60		
80	11.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.20

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (Ru (III)) =  $0.60 \times 10^{-6}$  M      Temperature  $35^{\circ}\text{C}$

(H <sub>2</sub> SO <sub>4</sub> ) M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.25	1.22
0.40	1.25
0.50	1.26
1.00	1.28
1.25	1.20
1.50	1.30

TABLE 5.21

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (Ru (III)) =  $0.20 \times 10^{-6}$  M      Temperature  $35^{\circ}\text{C}$

(H <sub>2</sub> SO <sub>4</sub> ) M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.20	3.26
0.30	3.36
0.40	3.32
0.50	3.31
0.70	3.40
1.00	3.20

TABLE 5.22

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (Ru (III)) =  $0.02 \times 10^{-6}$  M      Temperature  $35^{\circ}\text{C}$

(H <sub>2</sub> SO <sub>4</sub> ) M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.40	3.35
0.50	3.26
1.00	3.50
1.50	3.08
2.00	3.22
2.50	3.40
3.00	3.33



TABLE 5.23  
Temperature 35°C

[Ce (IV)]	= 10.00 X 10 <sup>-4</sup> M,	(Cyclopentanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.20 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
10	2.98		
20	3.60		
30	4.02		
50	4.82	9.50	3.28
70	5.62		
90	6.04		
120	7.20		
150	8.82		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.24  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Cyclopentanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.30 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $1.00 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
10	3.02		
20	4.92		
30	5.22		
50	6.90	9.50	3.34
70	7.92		
90	8.40		
120	9.90		
150	10.44		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.25  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclopentanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.40 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.00		
10	3.90		
20	4.62		
40	6.02	9.50	3.32
60	7.10		
80	8.20		
100	9.40		
120	10.02		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.26  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.22		
10	4.82		
20	5.80		
40	7.40	9.50	3.33
60	9.44		
80	11.40		
100	12.42		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.27  
Temperature 35°C

[Ce (IV)]	= 10.00 X 10 <sup>-4</sup> M,	[Cyclopentanol]	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.70 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.10		
10	4.24		
15	5.28		
30	6.00	9.50	3.41
45	7.18		
60	9.88		
75	9.88		
95	11.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.28  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclopentanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 1.00 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.40		
10	5.50		
15	6.65		
30	8.40	9.50	3.22
45	9.00		
60	10.44		
75	11.02		
95	12.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.29  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Cyclohexanol)	= $2.00 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.40 M,	(Ru (III))	= $0.02 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	5.12		
10	7.18		
15	9.02		
20	9.72	9.50	3.36
25	10.02		
30	11.02		
40	12.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.30  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 0.50 M,	(Ru (III))	= 0.20 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.25		
15	6.00		
25	7.52		
35	9.60	9.50	3.24
45	9.98		
55	10.04		
65	11.01		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 5.31  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 1.00 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.44		
5	4.94		
15	6.94		
25	8.46		
35	9.20	9.50	3.49
45	10.04		
55	11.04		
65	11.44		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.32  
Temperature 35°C

(Ce.(IV)) = $10.00 \times 10^{-4}$ M, (H <sub>2</sub> SO <sub>4</sub> ) = 1.50 M,	(Cyclohexanol) = $2.00 \times 10^{-2}$ M (Ru (III)) = $0.02 \times 10^{-6}$ M
--	--

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.44		
5	3.54		
15	5.54		
25	6.76		
35	7.76	9.50	3.09
45	8.80		
55	9.02		
65	9.74		
75	10.90		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.33  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Cyclohexanol)	= $2.00 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 2.00 M,	(Ru (III))	= $0.02 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.51		
5	3.67		
15	4.28		
25	5.44		
35	6.11	9.50	3.20
45	7.41		
55	8.29		
65	9.48		
75	10.92		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.34  
Temperature 35°C

(Ce (IV))	= 10.00 X 10 <sup>-4</sup> M,	(Cyclohexanol)	= 2.00 X 10 <sup>-2</sup> M
(H <sub>2</sub> SO <sub>4</sub> )	= 2.50 M,	(Ru (III))	= 0.02 X 10 <sup>-6</sup> M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	4.12		
15	5.74		
25	7.12		
35	8.10	9.50	3.41
45	8.68		
55	9.68		
65	10.02		
75	11.18		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 5.35

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclopentanol) =  $2.00 \times 10^{-2}$  M  
 (Ru (III)) =  $0.20 \times 10^{-6}$  M      Temperature 35°C

(H <sub>2</sub> SO <sub>4</sub> ) M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.20	3.28
0.30	3.34
0.40	3.32
0.50	3.33
0.70	3.41
1.00	3.22

TABLE 5.36

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Cyclopentanol) = $2.00 \times 10^{-2}$ M
(Ru (III))	= $0.02 \times 10^{-6}$ M	Temperature $35^{\circ}\text{C}$
(H <sub>2</sub> SO <sub>4</sub> ) M		(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0.40		3.36
0.50		3.24
1.00		3.49
1.50		3.09
2.00		3.20
2.50		3.41

The kinetic data of summarised tables of diols and cycloalcohols 5.20-5.22, 5.35-5.36 respectively clearly indicate that the values of  $(-dc/dt)$  do not differ from each other on changing the concentration of sulphuric acid in oxidation each glycols, and cycloalcohols, thus showing zero order dependence on sulphuric acid.

## **CHAPTER -VI**

### **DETERMINATION OF ORDER OF REACTION WITH RESPECT TO Ru (III) IN Ce (IV) OXIDATION OF DIOLS AND CYCLOALCOHOLS IN ACIDIC MEDIUM**

## 6- DETERMINATION OF ORDER OF REACTION WITH RESPECT TO Ru (III) IN Ce (IV) OXIDATION OF DIOLS AND CYCLOALCOHOLS IN ACIDIC MEDIUM

This chapter deals with the study of determination of order of the reaction with respect to Ru (III) chloride used as catalyst in the oxidation of ethylene glycol, propylene glycol, butylene glycol, cyclopentanol and cyclohexanol by oxidation of ceric sulphate. The reactions have been carried out at different concentrations of Ru (III) at fixed concentration of all other reactant at 35°C. The results of such experiment have been given in tables 6.1-6.6, tables 6.7-6.12, tables 6.13-6.18 tables 6.22-6.27 tables 6.28-6.33 in oxidation of ethylene glycol, propylene glycol, butylene glycol, cyclopentanol & cyclohexanol respectively.

The results of tables 6.1-6.6, 6.7-6.12, 6.13-6.18, 6.22-6.27, 6.28-6.33, have been summarised in tables 6.19, 6.20, 6.21, 6.34, 6.35 respectively.



TABLE 6.1  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.50 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.54		
10	3.40		
20	4.20		
40	4.82		
60	5.00	9.50	1.08
80	5.84		
110	5.30		
140	5.82		
170	6.66		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.2  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.54		
5	3.20		
10	4.30		
20	5.40		
30	6.22	9.50	1.24
40	7.82		
50	9.00		
60	11.52		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.3  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.80 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.00		
10	4.52		
15	5.26		
20	8.24	9.48	1.66
25	9.80		
30	11.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.4  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $1.00 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	3.40		
4	4.40		
6	5.00		
8	6.20	9.50	2.16
10	7.20		
12	8.40		
15	10.60		
20	12.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.5  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $1.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
2	4.00		
4	5.20		
6	6.22	9.50	2.52
8	7.20		
10	10.22		
12	12.18		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.6  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $1.40 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	4.38		
4	5.60		
6	6.18	9.48	3.20
8	7.60		
10	9.78		
12	12.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.7  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	2.98		
10	4.02		
20	5.60	9.48	2.04
30	6.26		
40	7.30		
70	8.40		
100	9.84		
130	11.22		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.8  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ] * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.22		
10	4.82		
15	5.22	9.50	3.40
20	6.24		
30	7.80		
40	8.90		
60	10.02		
80	11.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 6.9  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.30 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.00		
10	4.26		
15	5.64	9.50	5.10
20	6.84		
30	7.26		
40	9.25		
50	10.24		
60	11.62		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.10  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.40 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.20		
10	4.22		
15	5.60	9.50	6.72
20	6.26		
30	8.24		
40	10.10		
50	11.50		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.11  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.50 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.02		
10	4.26		
15	5.64	9.50	8.48
20	6.46		
25	7.26		
30	8.66		
35	10.24		
40	11.62		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.12  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	4.02		
4	5.22		
6	6.80	9.50	10.16
8	7.22		
10	8.52		
12	9.22		
14	10.22		
20	11.22		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.13  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.14 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
10	4.18		
20	5.22		
30	6.52	9.50	2.32
40	7.74		
50	8.34		
60	9.64		
70	10.00		
80	10.24		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.14  
Temperature 35°C

[Ce (IV)] =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.62		
10	4.58		
15	5.48	9.50	3.33
20	6.30		
30	7.38		
40	8.44		
60	9.32		
80	10.62		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.15  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.04 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.82		
10	5.28		
15	5.28	9.50	6.52
20	6.81		
25	7.51		
30	8.22		
35	8.38		
45	10.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.16  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.06 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.40		
10	4.80		
15	6.02	9.50	10.00
20	7.86		
25	9.02		
30	10.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 6.17  
Temperature 35°C

(Ce (IV))	= $10.00 \times 10^{-4}$ M,	(Butylene Glycol)	= $2.00 \times 10^{-2}$ M
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= $0.08 \times 10^{-6}$ M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
2	3.40		
4	4.00		
6	5.34	9.50	13.32
8	6.24		
10	7.00		
15	8.64		
20	9.02		
25	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.18  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.10 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
2	3.90		
4	4.60		
6	5.82	9.50	16.78
8	7.24		
10	8.60		
15	9.40		
20	10.00		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.19

$(\text{Ce (IV)}) = 10.00 \times 10^{-4} \text{ M},$        $(\text{Ethylene Glycol}) = 2.00 \times 10^{-2} \text{ M}$   
 $(\text{H}_2\text{SO}_4) = 0.50 \text{ M},$       Temperature  $35^\circ\text{C}$

$(\text{Ru (III)}) 10^{-6} \text{ M}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$	$10 K_1 = (-dt/dt)$ $\text{Sec}^{-1} (\text{Ru (III)})$
0.50	1.08	2.18
0.60	1.24	2.08
0.80	1.66	2.10
1.00	2.16	2.16
1.20	2.52	2.11
1.40	3.20	2.26

Average value of  $K_1 = 2.14 \times 10^{-1} \text{ Sec}^{-1}$

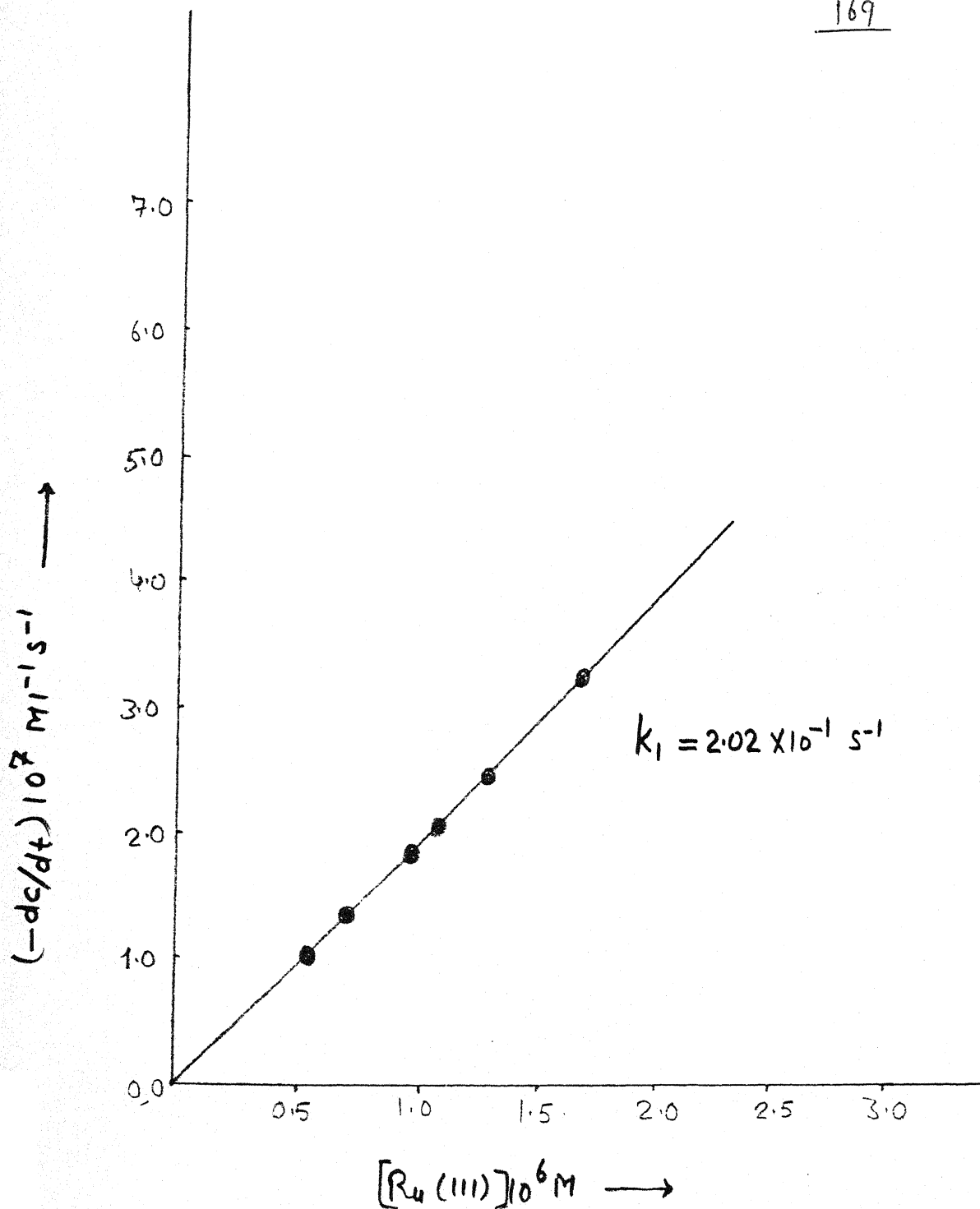


Fig. 6.1

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$  ,  $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$   
 $[\text{Ethylene glycol}] = 2.00 \times 10^{-2} \text{ M}$  temp. =  $35^\circ \text{C}$

TABLE 6.20

$[\text{Ce (IV)}] = 10.00 \times 10^{-4} \text{ M},$        $(\text{Propylene Glycol}) = 2.00 \times 10^{-2} \text{ M}$   
 $(\text{H}_2\text{SO}_4) = 0.50 \text{ M},$       Temperature  $35^\circ\text{C}$

$(\text{Ru (III)}) 10^{-6} \text{ M}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$	$10 K_1 = (-dt/dt)$ $\text{Sec}^{-1} (\text{Ru (III)})$
0.12	2.04	17.00
0.20	3.40	17.00
0.30	5.10	17.06
0.40	6.72	16.72
0.50	8.48	16.92
0.60	10.16	16.93

Average value of  $K_1 = 16.94 \times 10^{-1} \text{ Sec}^{-1}$

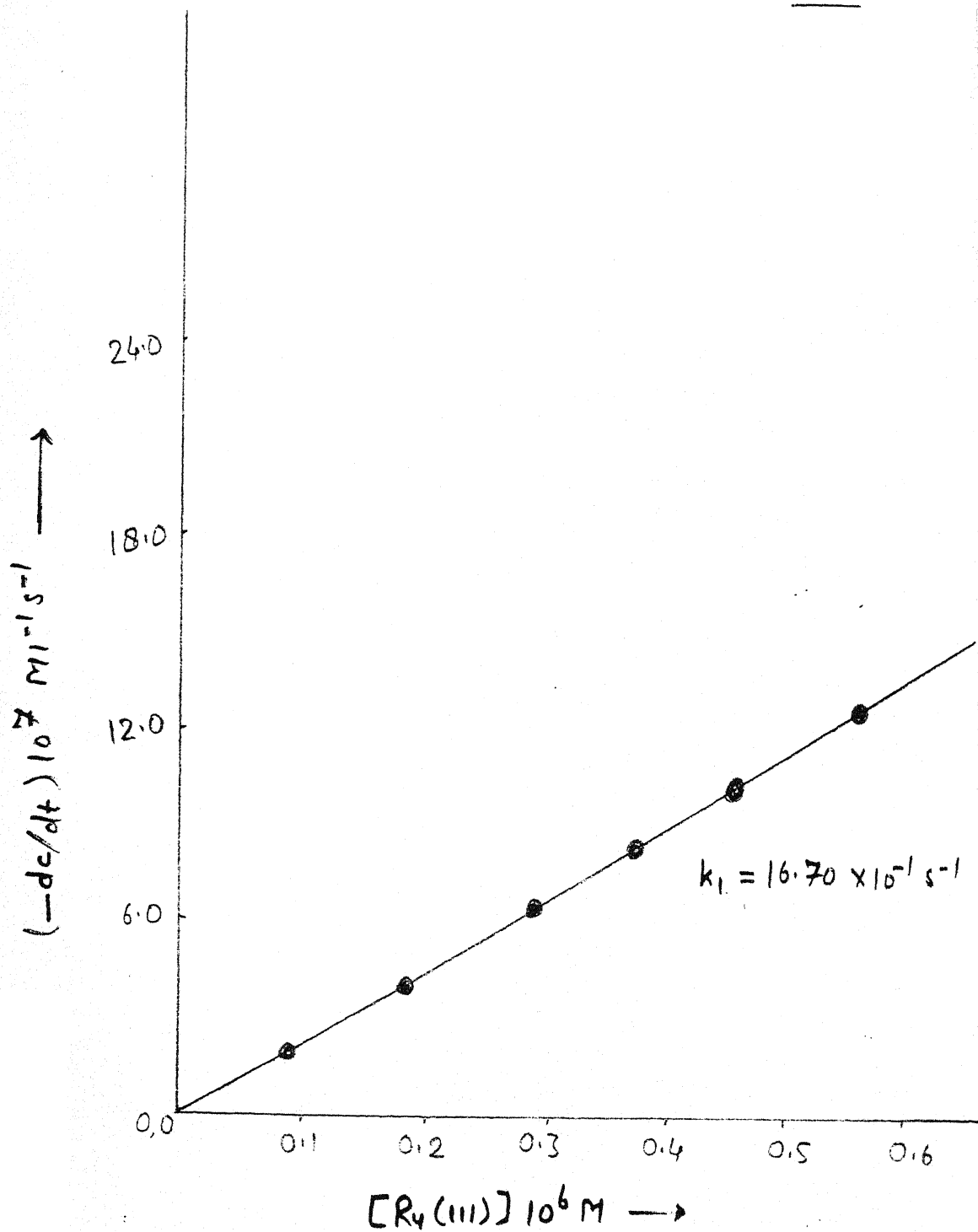


Fig. 6.2

$[\text{Ce}(\text{IV})] = 10.00 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.50 \text{ M}$

$[\text{Propylene glycol}] = 2.00 \times 10^{-2} \text{ M}$  temp. =  $35^\circ \text{C}$

TABLE 6.21

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 ( $\text{H}_2\text{SO}_4$ ) = 3.00 M,      Temperature  $35^\circ\text{C}$

(Ru (III)) $10^{-6}$ M	$(-\text{dc}/\text{dt}) 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$	$10 K_1 = (-\text{dt}/\text{dt})$ $\text{Sec}^{-1}$ (Ru (III))
0.014	2.32	16.71
0.020	3.33	16.65
0.040	6.52	16.25
0.060	10.00	16.66
0.080	13.32	16.63
0.10	16.78	16.80

Average value of  $K_1 = 16.62 \times 10^{-1} \text{Sec}^{-1}$

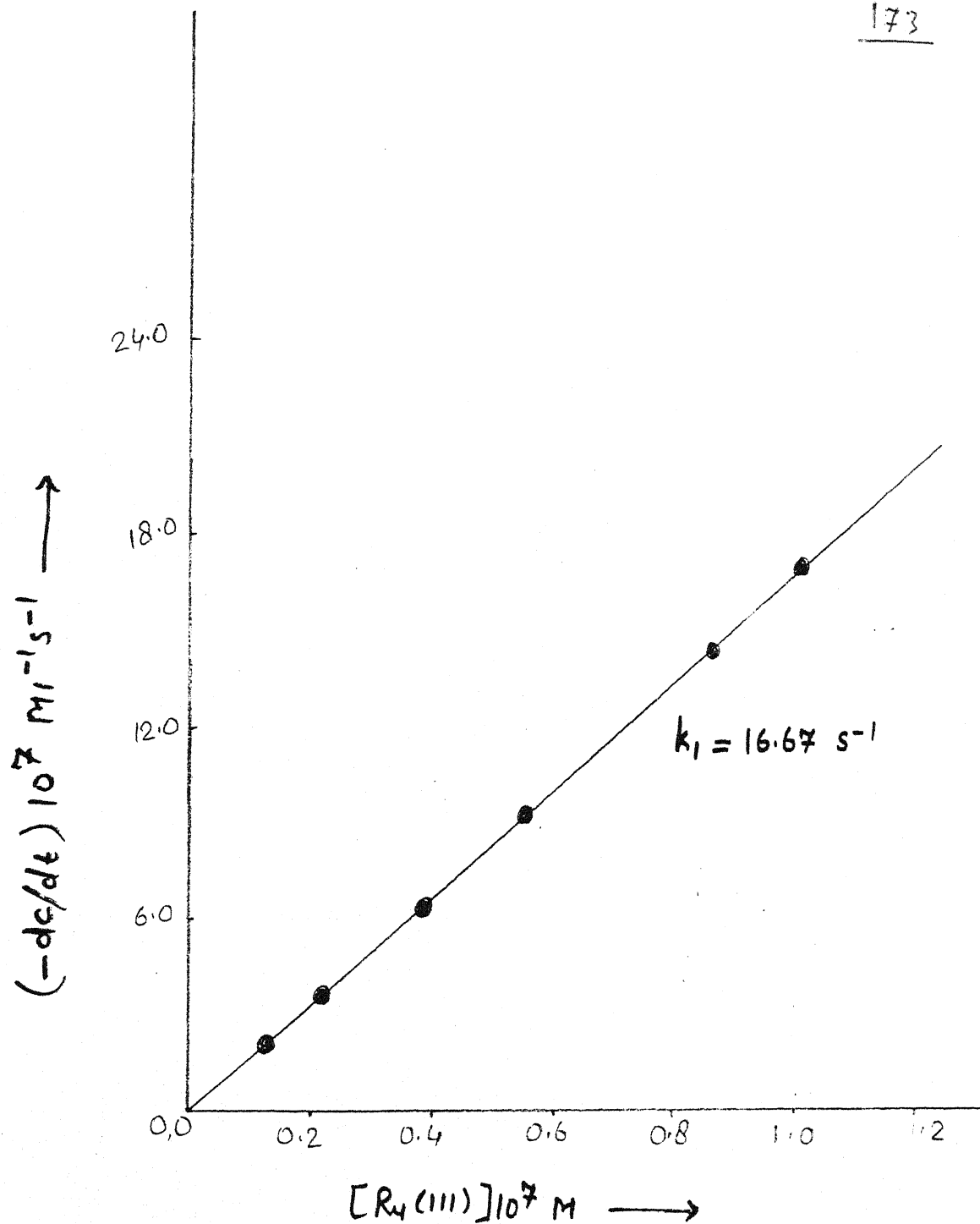


Fig. 6.3

$[\text{Ce(IV)}] = 10.00 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 3.00 \text{ M}$

$[\text{Butylene glycol}] = 2.00 \times 10^{-2} \text{ M}$ ,  $\text{temp.} = 35^\circ \text{C}$



TABLE 6.22  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,                      (Cypen) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,                                      (Ru (III)) =  $0.12 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.51		
5	3.00		
10	4.02		
20	5.60	9.50	2.05
30	6.26		
40	7.28		
60	8.44		
80	9.84		
100	11.20		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.23  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Cypen) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> (0.50 X 10 <sup>-3</sup> M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* 10 <sup>4</sup> M	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.20		
10	4.84		
20	5.21	9.50	3.41
30	6.21		
40	7.80		
60	8.94		
80	10.04		
100	11.02		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.24  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,                      (Cypen) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,                                      (Ru (III)) =  $0.30 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
5	3.02		
10	4.26		
15	5.60	9.50	5.11
20	6.80		
30	7.22		
40	9.22		
50	10.26		
60	11.60		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.25  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Cypen) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.40 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.44		
5	3.24		
15	4.20		
25	5.66	9.50	6.72
35	6.22		
45	8.22		
55	10.12		
65	11.52		
75	11.98		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.26  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Cypen) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M, (Ru (III)) =  $0.50 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.55		
5	2.95		
15	4.28		
25	5.64	9.50	8.45
35	6.44		
45	7.22		
55	8.62		
65	10.22		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.27  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,                      (Cypen) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,                      (Ru (III)) =  $0.60 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
2	4.02		
4	5.22		
6	6.84	9.50	10.15
8	7.26		
10	8.54		
12	9.20		
14	10.24		
16	11.20		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.28  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.01 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.44		
10	4.22		
20	5.20		
30	6.50	9.50	2.34
40	7.70		
50	8.32		
60	9.66		
70	10.02		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.29  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> )* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.50		
5	3.58		
10	4.58		
15	5.55	9.50	3.34
20	6.32		
30	7.42		
40	8.40		
50	9.32		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



TABLE 6.30  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.04 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce (SO <sub>4</sub> ) <sub>2</sub> ) <sup>*</sup> $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
5	3.78		
10	5.32		
20	7.46	9.50	6.54
25	8.20		
30	9.40		
35	10.10		
40	11.00		

\* - Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.31  
Temperature 35°C

$(\text{Ce (IV)}) = 10.00 \times 10^{-4} \text{ M},$ $(\text{H}_2\text{SO}_4) = 3.00 \text{ M},$		$(\text{Cyclohexanol}) = 2.00 \times 10^{-2} \text{ M}$ $(\text{Ru (III)}) = 0.06 \times 10^{-6} \text{ M}$	
Time (min)	ml of $\text{Ce (SO}_4)_2$ ( $0.50 \times 10^{-3} \text{ M}$ )	$(\text{Ce (SO}_4)_2) \times 10^4 \text{ M}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{ Sec}^{-1}$
0	2.54		
5	3.40		
10	4.84		
15	6.00	9.50	11.00
20	7.80		
25	9.00		
30	10.02		
40	10.33		
50	11.00		

\*- Conc. of Ceric Sulphate at which  $(-dc/dt)$  was determined.

TABLE 6.32  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.08 \times 10^{-6}$  M

Time (min)	ml of Ce (SO <sub>4</sub> ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	[Ce (SO <sub>4</sub> ) <sub>2</sub> ]* $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.48		
2	3.40		
7	4.04		
12	5.36	9.50	14.00
17	6.20		
22	7.04		
27	8.60		
32	9.00		
37	10.04		

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.33  
Temperature 35°C

(Ce (IV)) = $10.00 \times 10^{-4}$ M, ( $\text{H}_2\text{SO}_4$ ) = 3.00 M,	(Cyclohexanol) = $2.00 \times 10^{-2}$ M (Ru (III)) = $0.10 \times 10^{-5}$ M
--	--

Time (min)	ml of Ce ( $\text{SO}_4$ ) <sub>2</sub> ( $0.50 \times 10^{-3}$ M)	(Ce ( $\text{SO}_4$ ) <sub>2</sub> ) * $10^4$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0	2.52		
2	3.90		
7	4.60		
12	5.84	9.50	16.88
17	7.22		
22	8.64		
27	9.44		
32	10.00		
37	10.22		

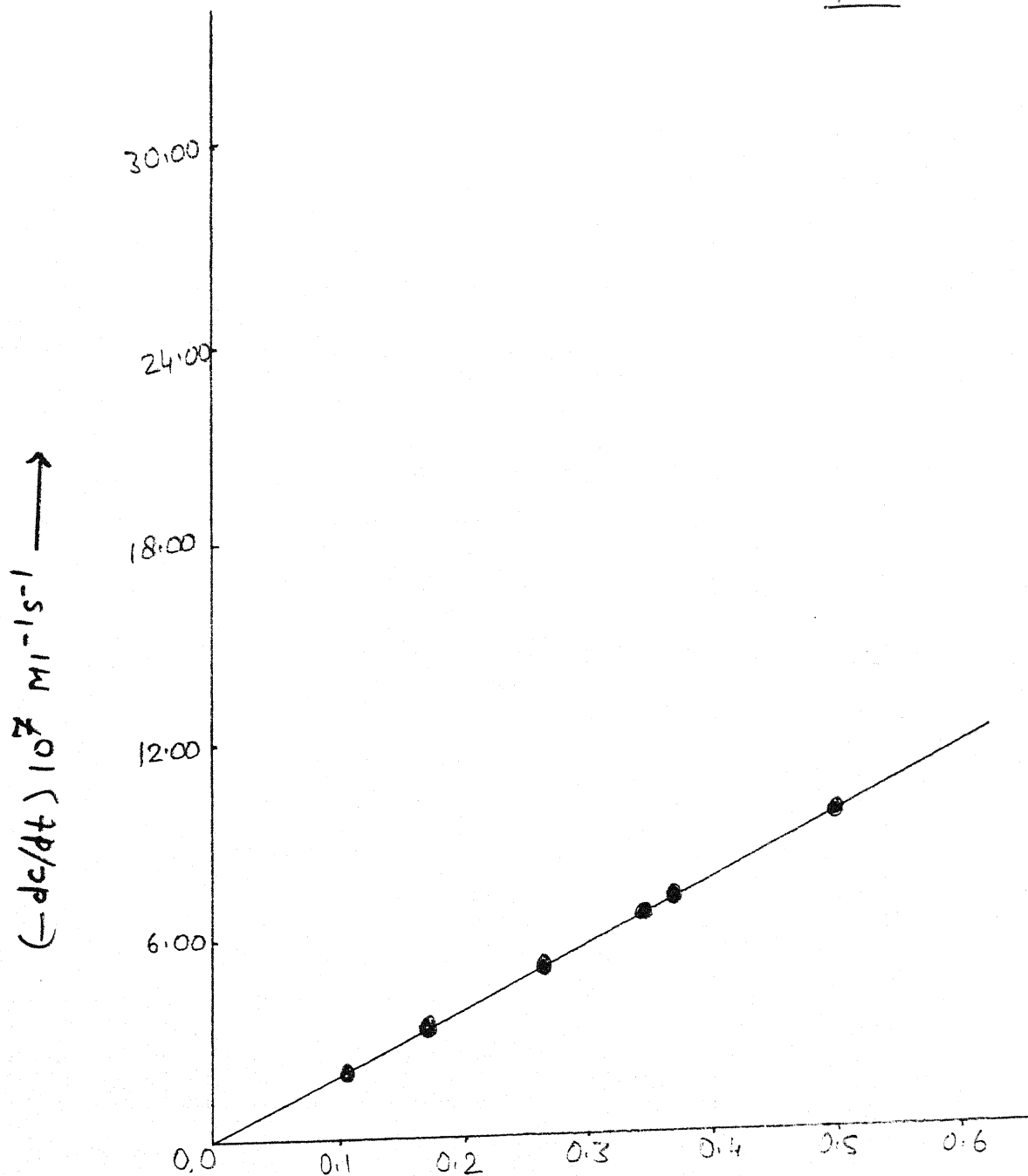
\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.

TABLE 6.34

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclopentanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      Temperature 35°C

(Ru (III)) $10^{-6}$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0.12	2.05
0.20	3.41
0.30	5.11
0.40	6.72
0.50	8.45
0.60	10.15

\*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.



$[Ce(III)] 10^6 \text{ M} \longrightarrow$   
 $[Ce(IV)] = 10.00 \times 10^{-4} \text{ M}$ ,  $[H_2SO_4] = 0.50 \text{ M}$   
 $[Cyp] = 2.00 \times 10^{-2} \text{ M}$ ,  $\text{temp.} = 35^\circ \text{C}$

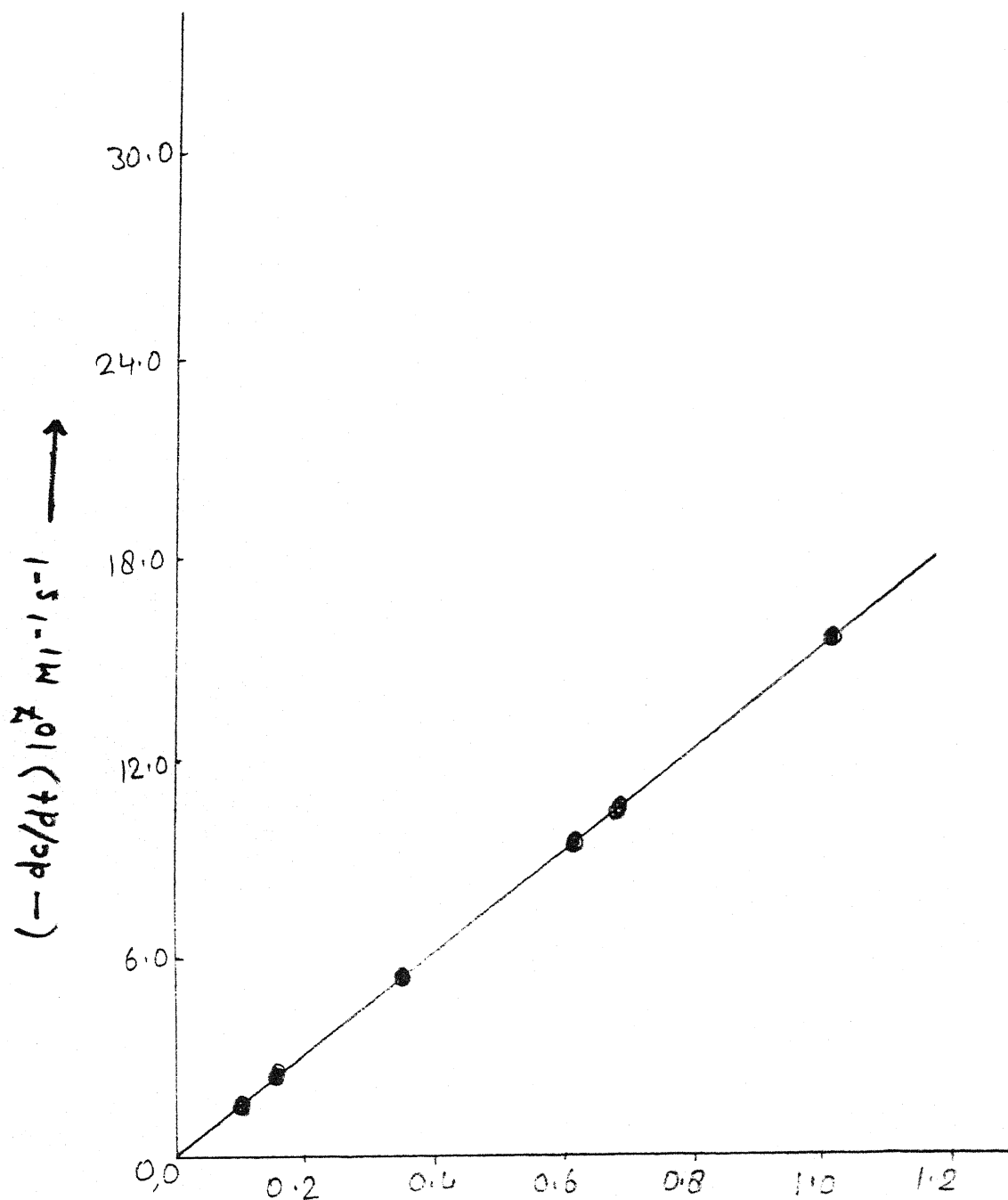
Fig. 6.4

TABLE 6.35

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      Temperature 35°C

(Ru (III)) $10^{-6}$ M	(-dc/dt) $10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>
0.01	2.34
0.02	3.34
0.04	6.54
0.06	11.00
0.08	14.00
0.10	16.88
*- Conc. of Ceric Sulphate at which (-dc/dt) was determined.	

The kinetic data of summarise tables 6.19-6.21, 6.34-6.35 indicates that the value of (-dc/dt) is directly proportional to the concentration of Ru (III) chloride in oxidation of each glycols and cycloalcols showing first order kinetics with respect to Ru (III) chloride.



$[R_4(III)] 10^7 \text{ M} \longrightarrow$

$[Ce(IV)] = 10.00 \times 10^{-4} \text{ M}$  ,  $[H_2SO_4] = 3.00 \text{ M}$

$[Cyclohexanol] = 2.00 \times 10^{-2} \text{ M}$  ,  $temp. = 35^\circ C$

Fig. 6.5



The above experimental finding is further confirmed when a plot between  $(-dc/dt)$  values and Ru (III) chloride concentration is drawn in case of oxidation of each of ethylene glycol (Fig 6.1), Propylene glycol (Fig 6.2) butylene glycol (Fig 6.3), cyclopentanol (Fig 6.4) cyclohexanol (Fig 6.5) is obtained. This confirms first order dependence of the reaction on Ru (III).

## **CHAPTER -VII**

### **STUDY OF EFFECT OF VARIATION OF IONIC STRENGTH ON THE VELOCITY OF REACTION**

## 7- STUDY OF EFFECT OF VARIATION OF IONIC STRENGTH ON THE VELOCITY OF REACTION

Here in the present chapter, the results obtained at various ionic strength of the medium maintained by addition of suitable amounts of sodium sulphate have been reported in table 7.1, 7.2, 7.3, 7.4, 7.5 in oxidation of ethylene glycol, propylene glycol, butylene glycol, cyclopentanol and cyclohexanol respectively in a consolidated manner. It is evident from the results of these tables that there is zero effect of ionic strength of the medium on the reaction. i.e the reactions under taken here are not influenced by changing the ionic strength of the medium of the reaction.

TABLE 7.1

Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Ethylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M, (Ru (III)) =  $0.60 \times 10^{-6}$  M

Na <sub>2</sub> SO <sub>4</sub> M	Ionic Strength $\mu \times M$	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.00	1.20	1.24
0.50	2.70	1.25
1.00	4.20	1.19
1.50	5.70	1.21
2.00	7.20	1.20

TABLE 7.2  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M, (Propylene Glycol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.40 M, (Ru (III)) =  $0.20 \times 10^{-6}$  M

Na <sub>2</sub> SO <sub>4</sub> M	Ionic Strength $\mu \times M$	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.00	1.50	3.33
0.50	3.00	3.26
1.00	4.50	3.36
1.50	6.00	3.30
2.00	7.50	3.31

TABLE 7.3  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Butylene Glycol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.02 \times 10^{-6}$  M

Na <sub>2</sub> SO <sub>4</sub> M	Ionic Strength $\mu \times M$	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.00	9.00	3.33
0.50	10.5	3.32
1.00	12.0	3.04
1.50	13.5	3.29
2.00	15.0	3.28

TABLE 7.4  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclopentanol) =  $2.00 \times 10^{-2}$  M  
(H<sub>2</sub>SO<sub>4</sub>) = 0.50 M,      (Ru (III)) =  $0.20 \times 10^{-6}$  M

Na <sub>2</sub> SO <sub>4</sub> M	Ionic Strength $\mu \times M$	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.00	1.50	3.34
0.50	3.00	3.25
1.00	4.50	3.36
1.50	6.00	3.30
2.00	7.00	3.32

TABLE 7.5  
Temperature 35°C

(Ce (IV)) =  $10.00 \times 10^{-4}$  M,      (Cyclohexanol) =  $2.00 \times 10^{-2}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 3.00 M,      (Ru (III)) =  $0.10 \times 10^{-4}$  M

Na <sub>2</sub> SO <sub>4</sub> M	Ionic Strength $\mu \times M$	(-dc/dt) 10 <sup>7</sup> ml <sup>-1</sup> Sec <sup>-1</sup>
0.00	9.00	3.33
0.50	10.50	3.35
1.00	12.00	3.04
1.50	13.50	3.30
2.00	15.00	3.30
2.50	17.00	3.40



## **CHAPTER -VIII**

### **EFFECT OF VARIATION OF TEMPERATURE ON THE RATE OF THE REACTION**

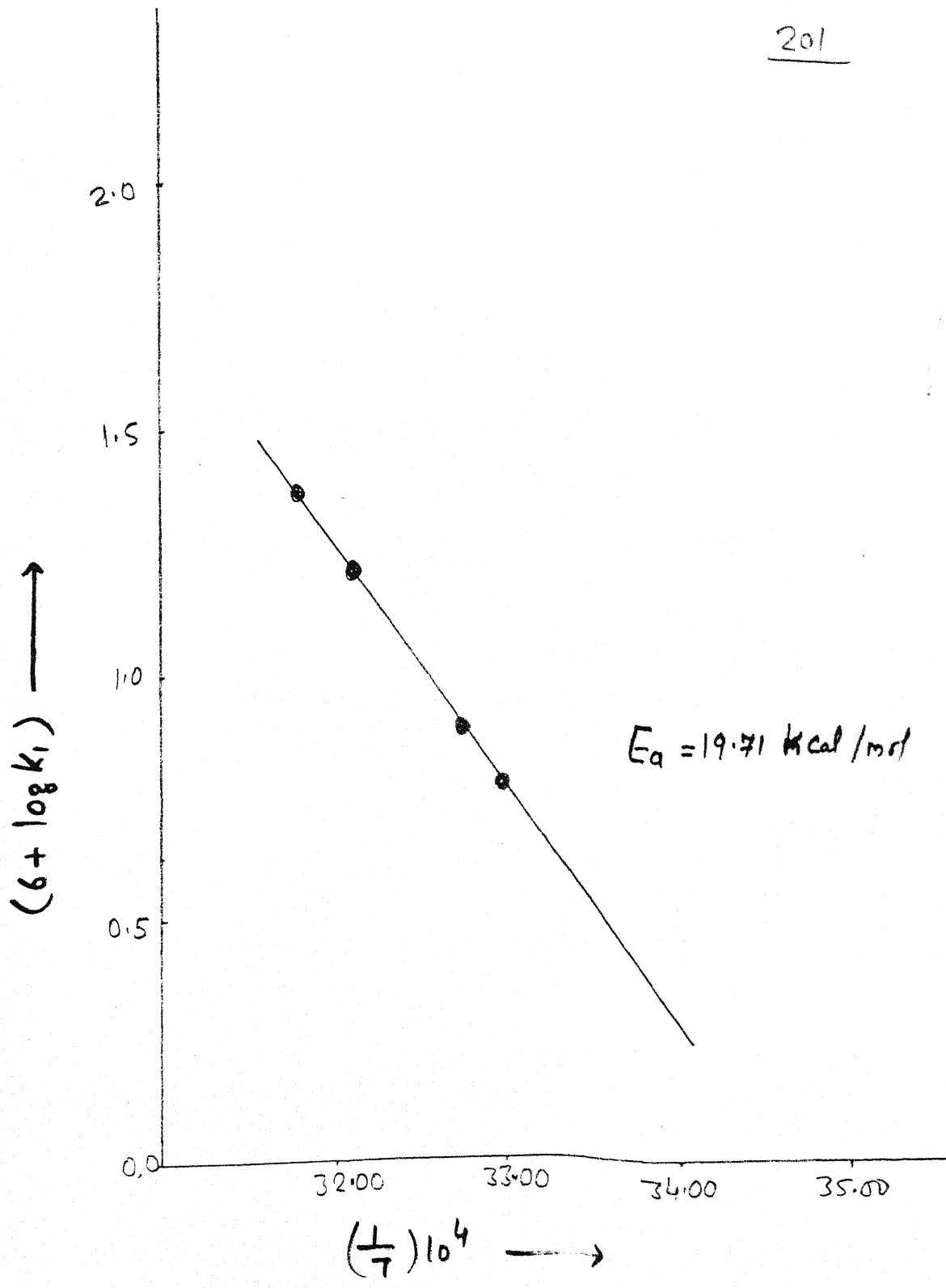
## 8- EFFECT OF VARIATION OF TEMPERATURE ON THE RATE OF THE REACTION

The following summarised tables contain the kinetic data collected at temperatures 30,35,40 and 45°C for ceric sulphate oxidation of ethylene glycol, propylene glycol, butylene glycol and cyclopentanol, cyclohexanol in presence of ruthenium (III) chloride as catalyst in acidic medium.

TABLE 8.1

(Ethylene Glycol) =  $2.00 \times 10^{-2}$  M      (Ce (IV)) =  $10.00 \times 10^{-4}$  M  
 (H<sub>2</sub>SO<sub>4</sub>) = 0.40 M,      (Ru (III)) =  $0.06 \times 10^{-6}$  M

Temperature 0°C	$(-dc/dt) 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>	$K_1 \times 10^{-5}$ Sec <sup>-1</sup>
30	0.74	0.37
35	1.25	0.62
40	1.90	0.95
45	3.00	1.50



Plot under conditions of Table 8.1

Fig 8.1

TABLE 8.2

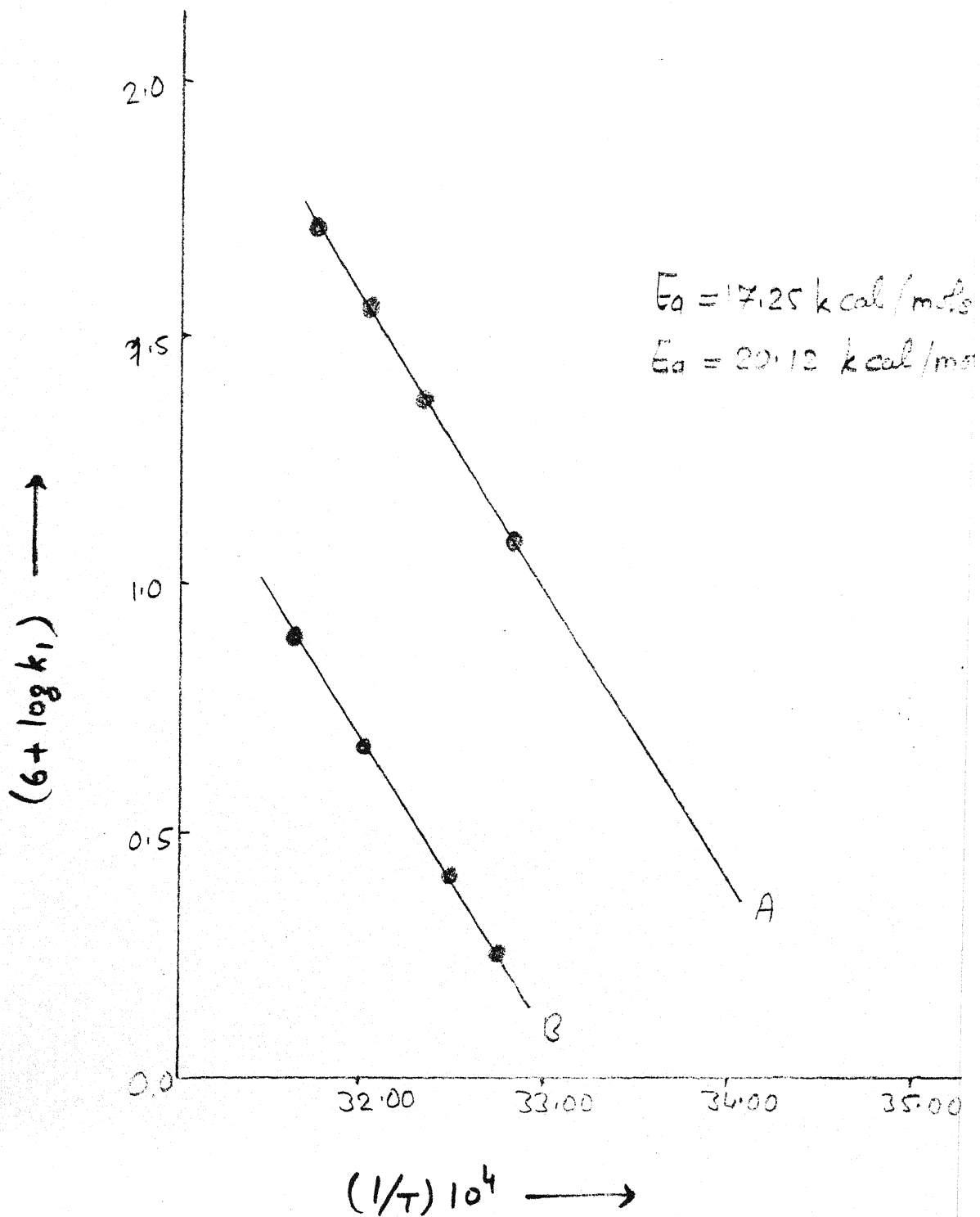
(Propylene Glycol)	= $2.00 \times 10^{-2} \text{ M}$	(Ce (IV))	= $10.00 \times 10^{-4} \text{ M}$
( $\text{H}_2\text{SO}_4$ )	= 0.50 M,	(Ru (III))	= $0.20 \times 10^{-6} \text{ M}$

Temperature $0^\circ\text{C}$	$(-dc/dt) 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$	$K_1 \times 10^{-5}$ $\text{Sec}^{-1}$
30	2.16	1.08
35	3.33	1.67
40	5.00	2.50
45	8.04	4.02

TABLE 8.3

(Butylene Glycol)	= $2.00 \times 10^{-2} \text{ M}$	(Ce (IV))	= $10.00 \times 10^{-4} \text{ M}$
(H <sub>2</sub> SO <sub>4</sub> )	= 3.00 M,	(Ru (III))	= $0.20 \times 10^{-3} \text{ M}$

Temperature 0°C	$(-dc/dt) 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>	$K_1 \times 10^{-5}$ Sec <sup>-1</sup>
30	1.98	0.99
35	3.33	1.67
40	5.16	2.58
45	8.24	4.12



Plot under conditions of table 8.2 (Propylene glycol) - A

Plot under conditions of table 8.3 (Butylene glycol) - B

Fig. 8.2

TABLE 8.4

(Cyclopentanol) = $2.00 \times 10^{-2} \text{ M}$	(Ce (IV)) = $10.00 \times 10^{-4} \text{ M}$
(H <sub>2</sub> SO <sub>4</sub> ) = 0.40 M,	(Ru (III)) = $0.06 \times 10^{-6} \text{ M}$

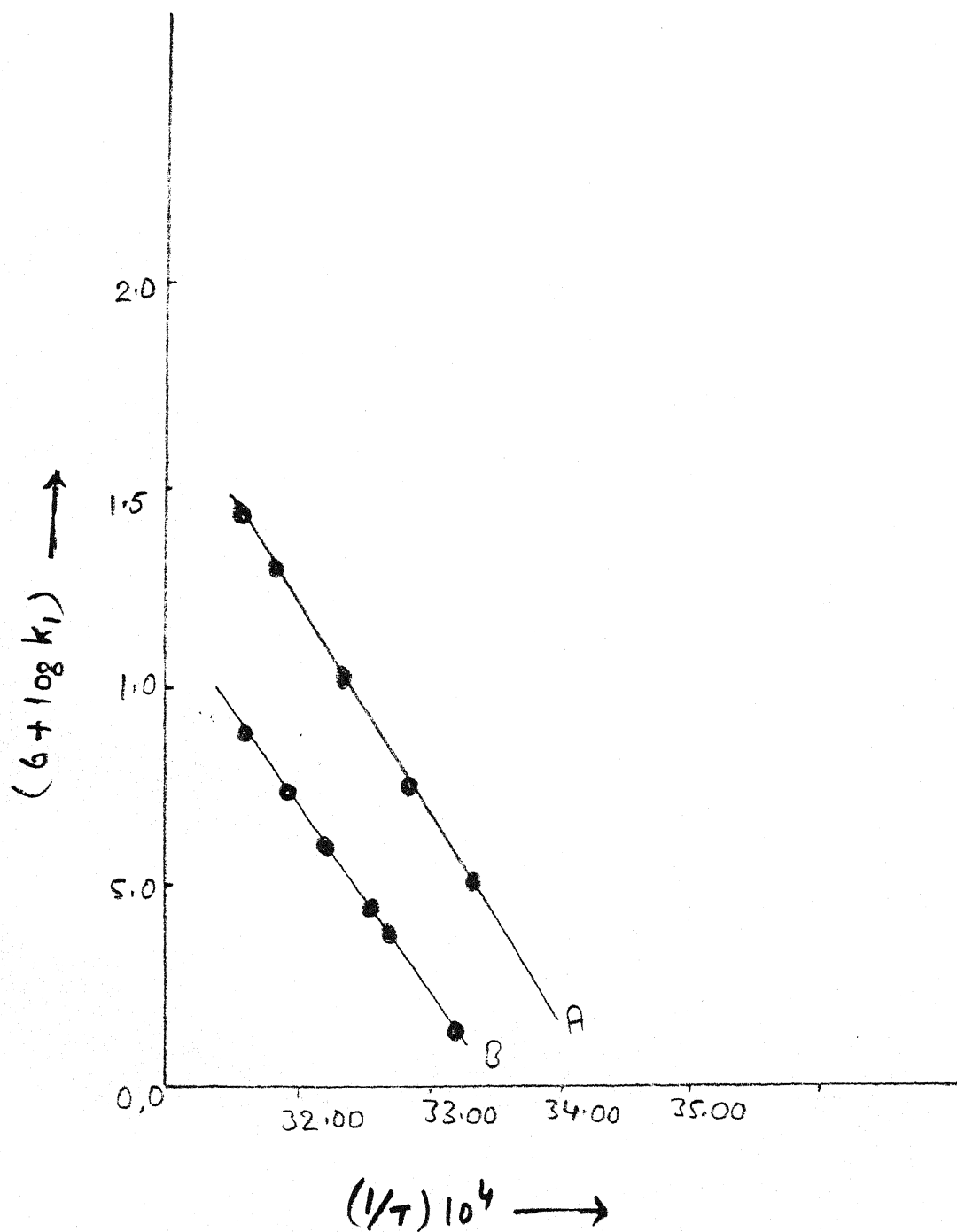
Temperature 0°C	$(-dc/dt) 10^7$ ml <sup>-1</sup> Sec <sup>-1</sup>	$K_1 \times 10^{-5}$ Sec <sup>-1</sup>
30	0.75	0.34
35	1.28	0.62
40	1.90	0.96
45	3.00	1.50



TABLE 8.5

(Cyclohexanol)	= $2.00 \times 10^{-2} \text{ M}$	(Ce (IV))	= $10.00 \times 10^{-4} \text{ M}$
( $\text{H}_2\text{SO}_4$ )	= 0.50 M,	(Ru (III))	= $0.20 \times 10^{-6} \text{ M}$

Temperature $^{\circ}\text{C}$	$(-\text{dc}/\text{dt}) 10^7$ $\text{ml}^{-1} \text{Sec}^{-1}$	$K_1 \times 10^{-5}$ $\text{Sec}^{-1}$
30	2.14	1.02
35	3.05	1.67
40	5.04	2.52
45	8.00	4.00



Plot between  $\log k_1$  &  $1/T$   
Cyclopentanone (A), Cyclohexanone (B)

Fig. 8.3

These reaction have been studied at  $30^{\circ}$ ,  $40^{\circ}$ , and  $45^{\circ}$  and with the help of these deservations, the value of energy of activation has been colculated.

The kinetic data of summarised tables has been produced graphically by plotting  $\log K_1$  against  $1/T$  (Fig 8.1, 8.2 and 8.3). A straight line with slope equal to  $E_a/2.203 R$  is dotained. Thus from the slope of the curve the value of  $E_a$  i.e. energy of activation is computed and the value of  $E_a$  i.e. energy of activation for oxidation of ethylene, propylene and butylene glycol have been obtained as 19.71, 17.25 and 20.12 k cal / mole respectively.

## **CHAPTER -IX**

### **INTERPRETATION OF THE RESULTS**

## 9.1 KINETIC RESULTS OBTAINED IN CERIC SULPHATE SOLUTION

The following identical observations have been noted in the title reactions.

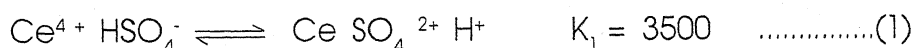
- (i) Zero - order dependence of the reactions on ceric sulphate has been observed.  
1st order in cyclicalcohol has been observed (Chapter-3)
- (ii) First - order kinetics with respect to each of glycols i.e. ethylene glycol, propylene glycol and butylene glycol has been observed.  
1st order with respect to cyclopentanol & cyclohexanol has been observed. (chapter-4)
- (iii) Negligible effect of variation of concentration of acid at constant concentrations of all other reactants have been observed.  
No effect in cyclicalcohols (chapter-5)
- (iv) First order dependence of all reactions on ruthenium (III) chloride concentration has been observed.  
1st order with respect to ruthenium (III) in cyclic alcohols. (Chapter -6)
- (v) Negligible effect variation of ionic strength of the medium on the reaction rate has been observed.  
No effect (Zero order) in cyclopentanol & cyclohexanol (chapter- 7)
- (vi) Addition of acetic acid to the reaction mixture (v/v) increased the reaction velocity constant.
- (vii) Increase of temperature significantly increased the reaction rate.

## 9.2 REACTIVE SPECIES OF CERIUM (IV) SULPHATE IN SULPHURIC ACID.

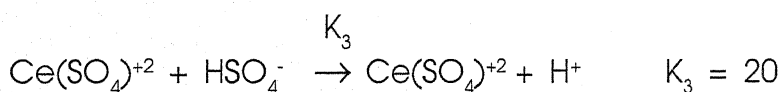
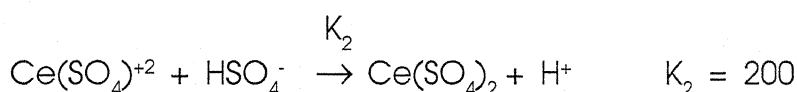
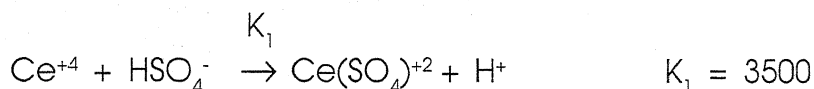
The reduction potentials of Ce (IV) - Ce (III) system in various concentrations of sulphuric, nitric and perchloric acids are 1.44, 1.61 and 1.70 volts at 25°C in the range of acidity. The decrease in potential in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  with increasing  $(\text{H}^+)$  as compared to  $\text{HClO}_4$  (in which potential increased with  $(\text{H}^+)$  is attributed to complexing of Cerium ions to form  $(\text{Ce}(\text{SO}_4)_4)^{4-}$  or  $(\text{Ce}(\text{SO}_4)_3)^{2-}$  and  $(\text{Ce}(\text{NO}_3)_6)^{2-}$ .

The increase in potential with increasing perchloric acid concentration is attributed to Ce (IV) hydrolysis product such as  $(\text{Ce}(\text{OH})_3)^{3+}$ ,  $(\text{CeO}(\text{OH})_2)^{4+}$  and  $(\text{Ce}_2\text{O}(\text{OH})_4)^{5+}$  appears to occur.

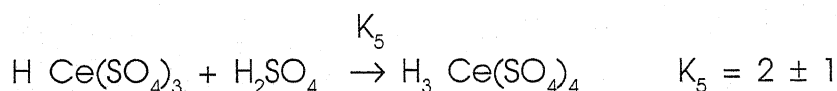
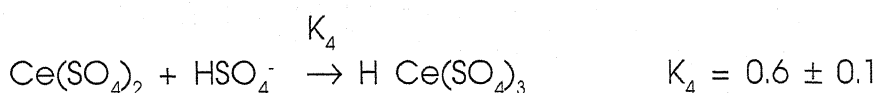
$E_0$  value in  $\text{H}_2\text{SO}_4$  was calculated to be +1.74 volts when account was made for bisulphate dissociation and following equilibria (1-4).



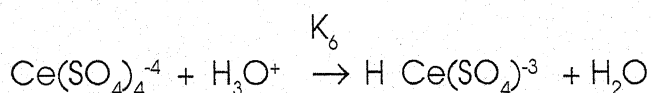
Cerium IV exists in various forms according to Hardwick and Robertson in 2 M sulphuric acid solution at constant ionic strength.

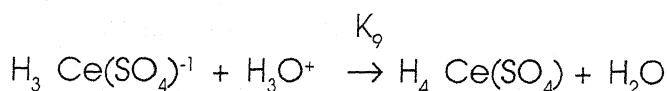
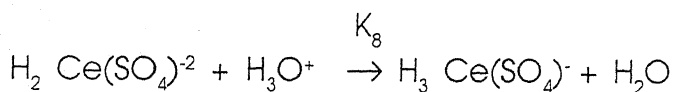
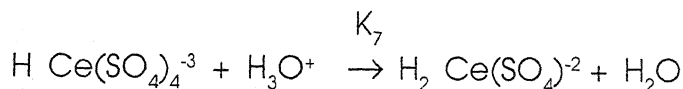


Bugaenko and Kuan have investigated the nature of Ce (IV) spectro photometrically in 0.1 M to 17.6 M sulphuric acid at 20°C are given below.

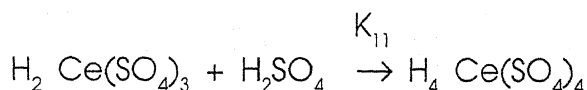
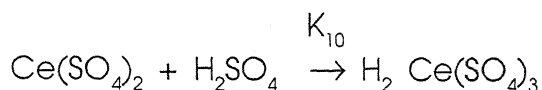


They have suggested that ceric sulphate and  $\text{H Ce}(\text{SO}_4)_3$  are the dominant species upto 2.6 molar sulphuric acid and  $\text{H}_2 \text{Ce}(\text{SO}_4)_2$  exists above 2 M sulphuric acid Hargreaves and Sutherland suggested the following equilibrium to explain the mechanism of certain reactions.





But the equilibrium constant have not been calculated though they have been useful in deriving some mechanism in addition to above equilibrium following equation have also been predicted-



In the oxidation of ethylene glycol with Ce (IV) sulphate Bhagwat etal and Methrota etal have suggested the reactive species as  $\text{Ce}(\text{SO}_4)_2$  on the other hand Mac Auley and Brubaker, Methrotra etal Guilberd etal have suggested the reactive species as  $\text{Ce}(\text{SO}_4)^{+2}$ , similarly Kaijermann and Rasmussen in the oxidation of pinacols by Ce (IV) sulphate have suggested  $\text{Ce}(\text{SO}_4)_3^{-2}$  as reactive species Gupta and Grover have suggested  $\text{Ce}(\text{OH})_2^{+2}$  as main reactive species in the oxidation of bengilic acid with Ce (IV) sulphate.

In the present studies since order with respect to Ce (IV) has been observed to be zero, hence it is involved in fast steps after rate determining step in the reaction. Hence whatever of the species is taken as reactive species, it would not matter as it shall be involved in



the fast step. Here for the sake of convenience and simplicity, Ce (IV) will be written as reactive species of Ceric sulphate in sulphuric acid medium.

The conclusion regarding the reactive species of Ce (IV) depends upon the observe experimental results.

### 9.3 REACTIVE SPECIES OF GLYCOLS IN SULPHURIC ACID.

In this thesis, reducing materials used are methyl glycol, ethylene glycol, propylene glycol and butylene glycol which have been used for their oxidation by ceric Sulphate in sulphuric acid medium. There are two possibilities of these glycols to be involved in the reaction. In the first place these glycols may be involved in the reaction as such i.e. in the neutral form and secondly as alternatively, these may be involved in the reaction in the protonated form. Since oxidation of these glycols have been observed to be independent of sulphuric acid concentrations, hence these glycols are involved in the reaction as such. Therefore, it is concluded that in the present investigation, glycols as such are reactive species.

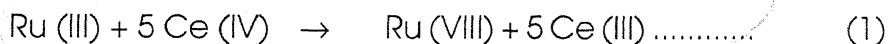
#### 9.4 REACTIVE SPECIES OF CYCLIC ALCOHOLS IN SULPHURIC ACID.

Cyclopentanol and cyclohexanol are used as reducing agent for the oxidation of ceric sulphate solution in sulphuric acid medium. These agent are involved in this reaction in two types first of all as such and secondly as their alternate.

These cyclic alcohols which are in their  $H^+$  form are independent of sulphuric acid concentration. This proved that they are involved in the reaction as such so these are the reactive species.

## 9.5 MECHANISM OF Ru (III) CATALYSED OXIDATION OF SOME GLYCOLS BY CERIC SULPHATE IN SULPHURIC ACID MEDIUM.

Ruthenium (III), when mixed with an excess of cerium (IV), is oxidised, rapidly and quantitatively ruthenium (VIII) as shown in eqn (I).



Ruthenium (III) show the same catalytic activity as ruthenium (III) when initially added to the reaction mixture and the rate of ruthenium (III) catalysed reaction was found to be in agreement with that of ruthenium (VIII) - catalysed reaction for the same ruthenium content. Therefore, in the present investigations of active species of the catalyst may be regarded as ruthenium (VIII). The ruthenium (III) catalysed oxidation of ethylene glycol, propylene glycol and butylene glycol follows similar kinetics. Zero - order dependence of rate on (Ce (IV)) clearly suggests its involvement in the fast steps. The reaction is also dependent on sulphuric acid concentrations. Therefore, the protonated form of glycols may be taken as the reacting species in these cases. As the rate of the oxidation in absence of catalyst is negligible, whereas in the presence of the catalyst the reactions show first -order dependence on (Catalyst) and (Substrate), an interaction between effective species of the catalyst and the protonated form of glycols appears to constitute the primary rate determining slow step.

The formation of a free radical as an intermediate has also been observed in the ruthenium (III) catalysed oxidation of some organic substances by Ce (IV).

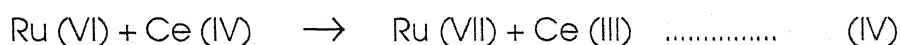
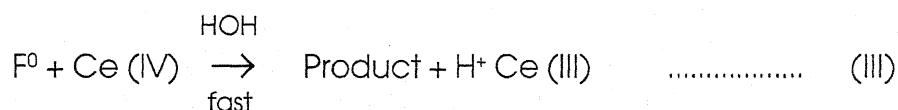
On the basis of above facts and experimental results, the

mechanism for the oxidation of ethylene glycol, propylene glycol and butylene glycol by ceric sulphate in the presence of Ru (III) chloride in Sulphuric acid medium may be proposed as follows where S represents glycols.

Since the oxidation of the glycols is independent of sulphuric acid concentrations hence natural glycol species is involved in the rate determining step. the mechanistic steps are suggested as



The forward reaction is rate determining step



Her nature of  $F^0$  (free radical) changes with change in th nature of glycol i.e.  $F^0$  may be  $^0C HO$  or  $^0CH_2 CHO$ , or both of these.

The conversion on Ru (VI) and Ru (VII) unstable species back to Ru (VIII) with oxidation Ce (IV) in th fast steps has been reported in literarure. The rate law equation for oxidation of glycols under experimental conditions in general may be represented as follows.

$$\frac{-d(Ce(IV))}{dt} = K_1 (S) (Ru(VIII)) \dots\dots\dots (2)$$

Since  $(\text{Ru (VIII)}) = (\text{Ru (III)})$  as earlier reported, hence equ. (2) may be written as

$$\frac{-d (\text{Ce (IV)})}{dt} = K_1 (\text{S}) (\text{Ru (III)}) \dots\dots\dots (3)$$

The above mechanism and rate law derived on its basis also finds support from zero- dependence of ionic strength of the medium as step (1) ie rate determining step involves an interaction between a dipole (i.e. glycols) and a positively charged species i.e.  $\text{Ru (VII)}$ .

The rate law (3) thus clearly explains

- (1) Zero order dependence on  $\text{Ce (IV)}$
- (2) Zero order dependence on  $(\text{H}^+)$
- (3) First order kinetics with respect to glycols .
- (4) First order dependence of reactions on  $\text{Ru (III)}$  chlorid.
- (5) Negligible effect of variation of ionic strength of the medium on the rate of oxidation of glycols.

Hence proposed mechanism seems to be correct.

## 9.6 MECHANISM OF Ru (III) CATALYSED OXIDATION OF SOME CYCLIC ALCOHOLS BY CERIC SULPHATE IN SULPHURIC ACID MEDIUM.

According to informal investigations the mechanism of Ru (III) catalysed oxidation of cyclic alcohols have been given spectrophotometrically.

$$\frac{-d(\text{Ce (IV)})}{dt} = K_1 (\text{S}) (\text{Ru (III)})$$

Above rate law equation clearly indicates that.

- (1) 1st order dependence of Ce (IV)
- (2) Zero order dependence of (H<sup>+</sup>)
- (3) 1st order dependence with respect to cyclic alcohols.
- (4) 1st order dependence of reactions on Ru (III) chloride.

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